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THIN FILM PERSONAL DOSIMETERS FOR DETECTING TOXIC PROPELLANTS

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MAGNA CORPORATION

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FOREWORD

This investigation was made by the Research and Development Division, Magna Corporation, under USAF Contract No. AF33(615)-1751. The contract, "Thin Film Personal Dosimeter for Detecting Toxic Propellants," was initiated under Project No. 6302, "Toxic Hazards of Propellants and Materials," Task No. 630203, "Identification of Toxic Materials," with Mr. S. F. Brokeshoulder as contract monitor for AMRL.

This is the final report for the project and covers work conducted from 15 April 1964 through 15 April 1965. Magna Corporation has become a part of TRW Systems Group since the initiation of this contract; as a result, the report bears the TRW designation 6302-6001-R0000.

This technical report has been reviewed and is approved.

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ABSTRACT

A portable system for the detection of low concentrations of nitrogen tetroxide (N_2O_4), fluorine (F_2), and unsymmetrical dimethylhydrazine (UDMH) in air has been developed. The detection system is based upon the change of electrical resistivity of thin metal films when exposed to these gases. Silver metal films coated with appropriate salts proved to be applicable to the detection of all three gases. However, the following metal films were found to be optimum: for N_2O_4 , silver; F_2 , copper; and for UDMH, gold. Using the best film and salt combinations found to date, N_2O_4 could be monitored over the range of 0.1 to 50 ppm, F_2 over the range 1.0 to 100 ppm, and UDMH over the range 10 to 1000 ppm, with a standard deviation of about 20 percent. The effects of temperature over the range 50° to 90°F and of humidity from 10 to 90 percent R. H. on the response characteristics of the thin film sensors were found to be significant.

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SECTION I

INTRODUCTION

The corrosion of metal surfaces when exposed to an environment containing reactive gases has led to the development of a compact system for the detection of low concentrations of rocket propellant vapors in the air. Using thin metal films as sensors, a breadboard instrument has been constructed which can detect nitrogen tetroxide and fluorine in air at concentrations below 5 ppm in less than 5 minutes. Vapors of unsymmetrical dimethyl hydrazine (UDMH) are detectable at 10 ppm in less than 5 minutes, and there is evidence that this sensitivity can be improved by an order of magnitude or better. The thin film sensors are relatively inexpensive and simple in operation. In addition, they are solid state devices, which makes them more reliable and simpler to package than fluid state devices.

The use of thin metal films as analytical tools was made attractive by the development of the electrical resistance method of measurement. The electrical resistance method makes use of the fact that metals and alloys have much lower specific electrical resistances than their chemical reaction products. Thus, the electrical resistance of a metal conductor depends on the cross-sectional area of unreacted metal. Any decrease in thickness of the metal due to a chemical reaction with a propellant vapor results in a proportional increase in electrical resistance.

The electrical resistance method uses a special sensor probe exposed to the environment under study. The metal loss on the probe is followed by measuring the change in resistance of the probe. The sensor probe consists essentially of an exposed metal specimen that is made part of an electrical bridge circuit. Metal loss of the exposed specimen is measured by reference to an adjacent, noncorroding reference specimen. The associated instrumentation measures the ratio of the electrical resistance of the exposed specimen and the reference specimen. It is this self-compensating feature of the bridge circuit that defines the sensitivity and versatility of the method.

The sensor consists of the measuring element and reference element plus electrical connections. The measuring and reference elements consist of the selected metal film deposited onto a plastic substrate. In use, the reference element and electrical connections are coated with a relatively impervious material to provide protection, leaving only the measuring element exposed to the atmosphere.

The electrical resistance method is outstanding for detecting and measuring metal loss or reaction, without disturbing the environment. Also by varying the thickness and thus the cross-sectional area of metal used in the exposed specimen, a wide range of sensitivity can be achieved. Using a metal specimen 0.004 inch thick, for example, an environment that will cause a metal loss of 10 mils per year will cause a change of 1 micro-inch per hour, which can be easily monitored by commercially available instrumentation. By decreasing the initial metal thickness—by using, for example, very thin metal films (1000 Å or less in thickness)—metal loss corresponding to a billionth of an inch can be measured.

This development program was concerned with selection of a metal film that would react slowly in air under ambient conditions but would react rapidly in the presence of very low concentrations of the selected propellant vapor. Most metals form a protective oxide or other metal salt film when exposed to air or to a reactive chemical. However, it has been shown that metal surfaces that are attacked only slowly in a given environment will be grossly corroded when contaminated with foreign material. In air, the contaminated area will corrode faster than the clean metal surface. By contaminating, or "sensitizing," metal films with particular treatments, the protective films that form can be broken down. This permits the process of corrosion, or metal loss, to continue as long as either the metal or the substance causing corrosion remains.

The result of the study described in this report has been the development of a small, lightweight breadboard model of an instrument capable of detecting low concentrations of vapors of nitrogen tetroxide, fluorine, and UDMH. Included in the report are the performance characteristics of each of the sensors, the methods of fabrication and sensitization of the films, and the effect of the environmental conditions of temperature and humidity on the response of the sensors. These results represent the present state of the art.

SECTION II

EXPERIMENTAL PROCEDURE

METHOD OF MEASUREMENT

The method of measurement is based on the change in electrical resistance of a thin metal film conductor as it reacts with a vapor. The electrical resistance R of a conductor is inversely proportional to its cross-sectional area A ; i. e. ,

$$R = \rho \frac{L}{A}, \quad (1)$$

where ρ , the resistivity, is a constant for the particular material and L is the length of the resistive path.

The cross-sectional area term A of equation 1 is the product of the film width W and thickness h .

$$A = hW \quad (2)$$

$$h = \frac{\rho L}{WR}, \quad (3)$$

and the change in thickness from the initial to the final value is

$$h_i - h_f = \frac{\rho L}{WR_i} - \frac{\rho L}{WR_f}, \text{ or } \Delta h = \frac{\rho L}{W} \left(\frac{1}{R_i} - \frac{1}{R_f} \right), \quad (4)$$

where the subscripts i and f refer to the initial and final values (before and after exposure). This quantity, Δh , represents the amount of metal that has reacted with the vapor and is therefore the parameter that best represents the concentration of vapor \times time of exposure.

A "Corrosometer," a commercially available bridge circuit, was used to measure the relative resistance of the thin film sensors. This instrument gives a dial reading D which is related to the ratio of the measuring film resistance R to the reference film resistance R_o by the following equation:

$$\frac{R}{R_o} = \frac{a}{b - D}, \text{ or } R = \frac{R_o a}{b - D}, \quad (5)$$

where a and b are circuit constants.

Substituting equation 5 for the values of R_i and R_f in equation 4 gives

$$\Delta h = \frac{\rho L}{W} \left(\frac{1}{\frac{R_o a}{b - D_i}} - \frac{1}{\frac{R_o a}{b - D_f}} \right), \quad (6)$$

which simplifies to

$$\Delta h = \frac{\rho L}{WR_o a} (D_f - D_i). \quad (7)$$

Since the resistivity ρ of a vacuum deposited film is not necessarily the same as that of the bulk metal, this term cannot be given an absolute value but can be included in a proportionality constant along with the path length, path width, and circuit constant a . If these factors are grouped into a proportionality constant and $\Delta h'$ is defined as a relative measure of average thickness loss occurring between the initial and final dial readings (D_i and D_f), the equation reduces to

$$\Delta h' = \Delta h \frac{aW}{\rho L} = \frac{D_f - D_i}{R_o}. \quad (8)$$

This relationship normalizes the response of films with different initial resistances, making it possible to compare the results of tests in which films of more than one initial resistance are used. The term $\Delta h'$ is referred to as "exposure factor" throughout this report and is used to evaluate the results of different tests on an equivalent basis. The exposure factor is a measure of the exposure of the film to a vapor.

PREPARATION OF SENSORS

The substrates used in this program consisted of 1-1/2 x 1-1/16 x 1/16 inch pieces of copper-coated phenolic plastic circuit board material. All of the copper, except areas used for electrical contacts, was etched away to leave a clean plastic surface for deposition of the metal film.

Vacuum deposition of the thin metal films was performed by Herron Optical Co., Los Angeles, by the following procedure. The substrates were vapor degreased and placed in a vacuum chamber, which was then evacuated until there was no significant gassing of the phenolic substrates,

and a constant pressure of 10^{-4} mm mercury was obtained. The metals used to make the films were evaporated from a tungsten wire filament onto the surfaces of the substrates, where they condensed to produce the metal films.

After deposition, a resistive path was formed on the sensor by sand-blasting through a mask to etch thin, nonconductive lines in the metal film. Figure 1 shows a sensor prepared in this manner. The reference sides of the sensors are coated to protect them from the gas being detected. Of several coatings evaluated for this purpose, Cellophane tape proved to be both the most nonreactive and most convenient to apply; therefore it was used throughout the program.

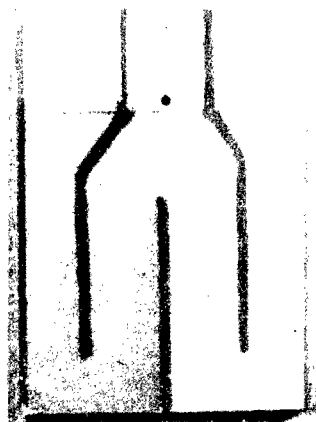


Figure 1. Thin Film Sensor

To obtain the required constancy of film resistance, a test strip of substrate material, to which electrical leads were soldered, was simultaneously vacuum deposited with each batch of substrates. Its resistance was monitored while deposition of the films was in progress. When the desired resistance was attained, deposition was stopped. In addition, the substrates were mounted on a rotating platform within the vacuum chamber so as to uniformly expose all substrates to the metal source. The standard deviation of resistance for films prepared in this manner was

19 percent for a batch of 80 films. Groups of untreated metal films within each batch were selected such that the standard deviation of the resistance was within 7 percent of the mean.

SENSITIZER APPLICATION

The metal films on the exposed section were treated with various chemicals to increase their sensitivity. Early in the program, the chemicals were applied by either dipping the films in aqueous solutions or spraying the films with an aqueous solution of the chemicals followed by air drying. Later in the program methanol solutions were used. In this case, the film was dipped into the methanol solution and removed, the excess solution was allowed to drain off slowly (about 3 to 5 sec), and the film was then flash-dried by placing it in the air stream of a heat gun for approximately 5 seconds.

TEST CHAMBERS

Tests to determine the air oxidation rate of sensors and to evaluate protective coating materials for the reference arm were conducted using the test chamber shown in figure 2. This test chamber was fabricated of 1/2 inch thick acrylic plastic and had an internal volume of 1.65 cubic feet. Thirty-two test sites were available inside the chamber, each equipped with feedthrough electrical connections to allow external connection of the "Corrosometer" to each film. A gas inlet and outlet were placed at opposite ends of the chamber so that filtered and KOH-scrubbed air could be flowed through the chamber. A 6-inch hole and cover in the front of the chamber provided easy access to the test sites for sensor replacement.

A smaller, glass chamber was used to expose the films to known concentrations of UDMH and N_2O_4 , while a polyethylene chamber of design similar to the glass chamber was used for fluorine. These small chambers contained a gas inlet tube leading to a circular Teflon ring at the bottom of the chamber. This ring contained small holes on the bottom surface to disperse the incoming gas. The outlet tube was at the top of the chamber, centrally located between the films. Four film holders were contained in each chamber.

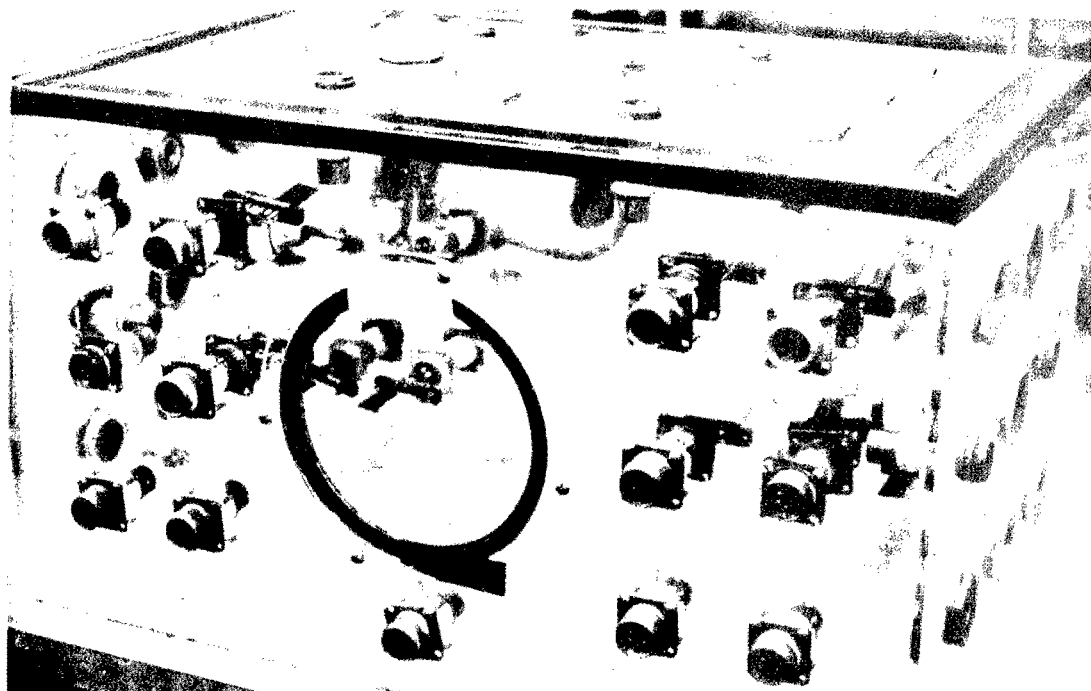


Figure 2. Thirty-Two Position Test Chamber

PREPARATION OF TEST VAPORS

The UDMH flow apparatus and test chamber are shown schematically in figure 3 and photographically in figure 4. A diluted source of UDMH vapor was obtained by bubbling a small stream of dry nitrogen through pure liquid UDMH. From a knowledge of the vapor pressure of UDMH as a function of temperature, a vapor of any desired UDMH concentration could be provided by controlling the temperature of the UDMH. A larger stream of clean air at a fixed humidity flowing at a fixed rate was mixed with the UDMH-N₂ stream to give the desired concentration of UDMH vapor in the test chamber.

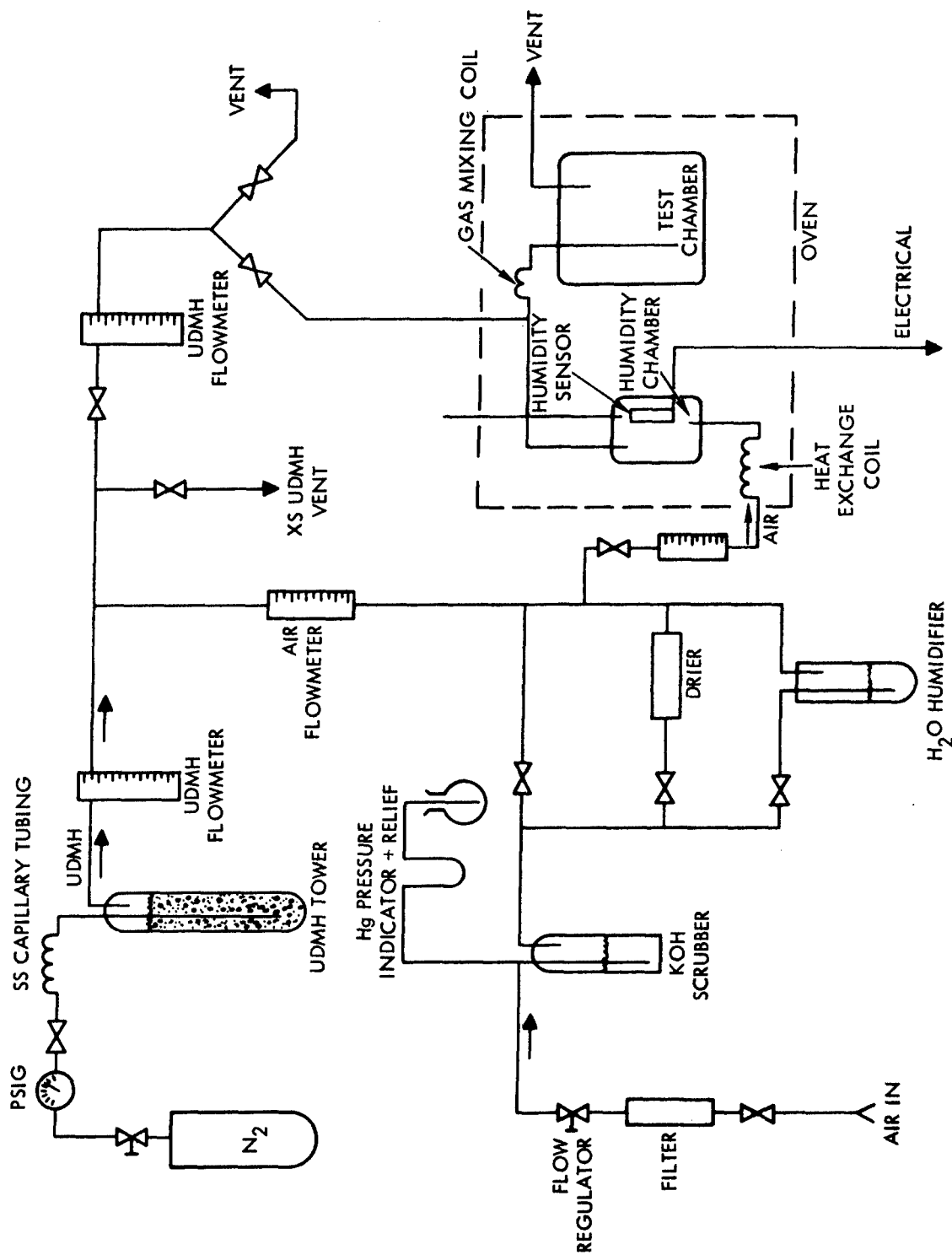


Figure 3. UDMH Flow Apparatus

Diagrams and photographs of the N_2O_4 and F_2 flow systems are shown in figures 5, 6, 7, and 8. The N_2O_4 system is similar to the UDMH apparatus described except for the source of N_2O_4 vapor. A source of diluted N_2O_4 vapor was prepared by placing approximately 300 ml of pure liquid N_2O_4 into a gas cylinder and pressurizing the cylinder to 900 psi with dry N_2 . When the cylinder is placed in a temperature-controlled bath, the composition of the effluent from the cylinder is related to the vapor pressure of N_2O_4 at that temperature. At the temperature used (0°C), the gas from the cylinder at ambient pressure was about 1 percent N_2O_4 in N_2 . This mixture was then further diluted with air, as in the UDMH system.

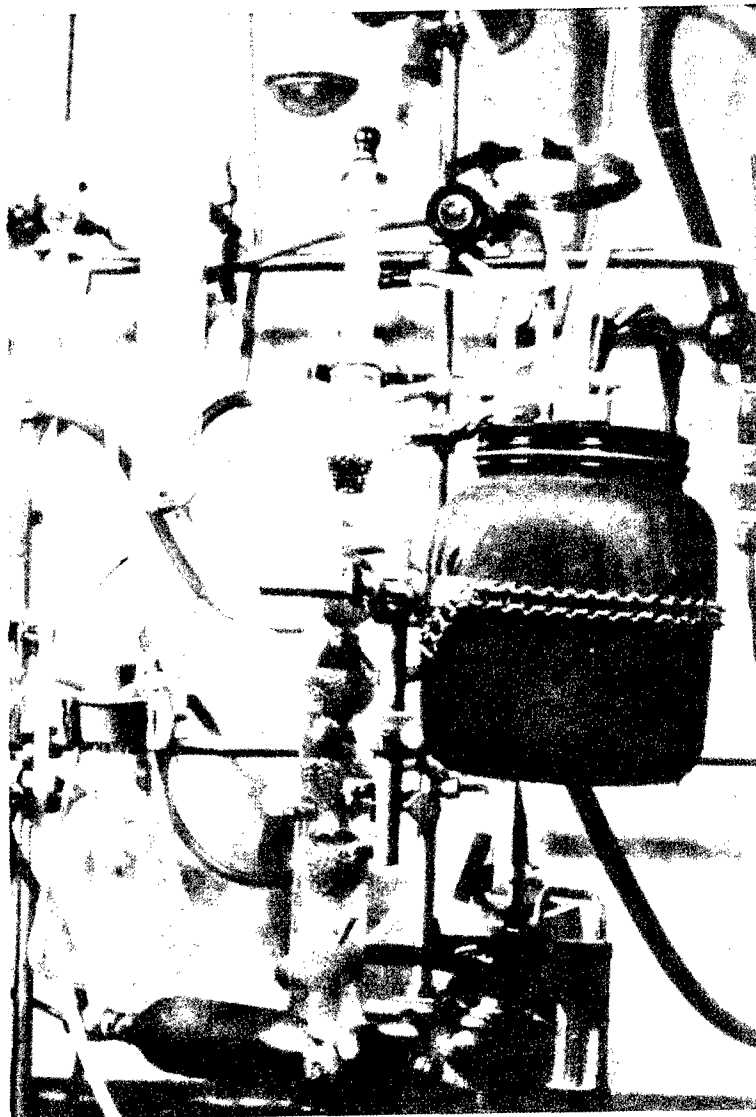


Figure 4. UDMH Test Apparatus

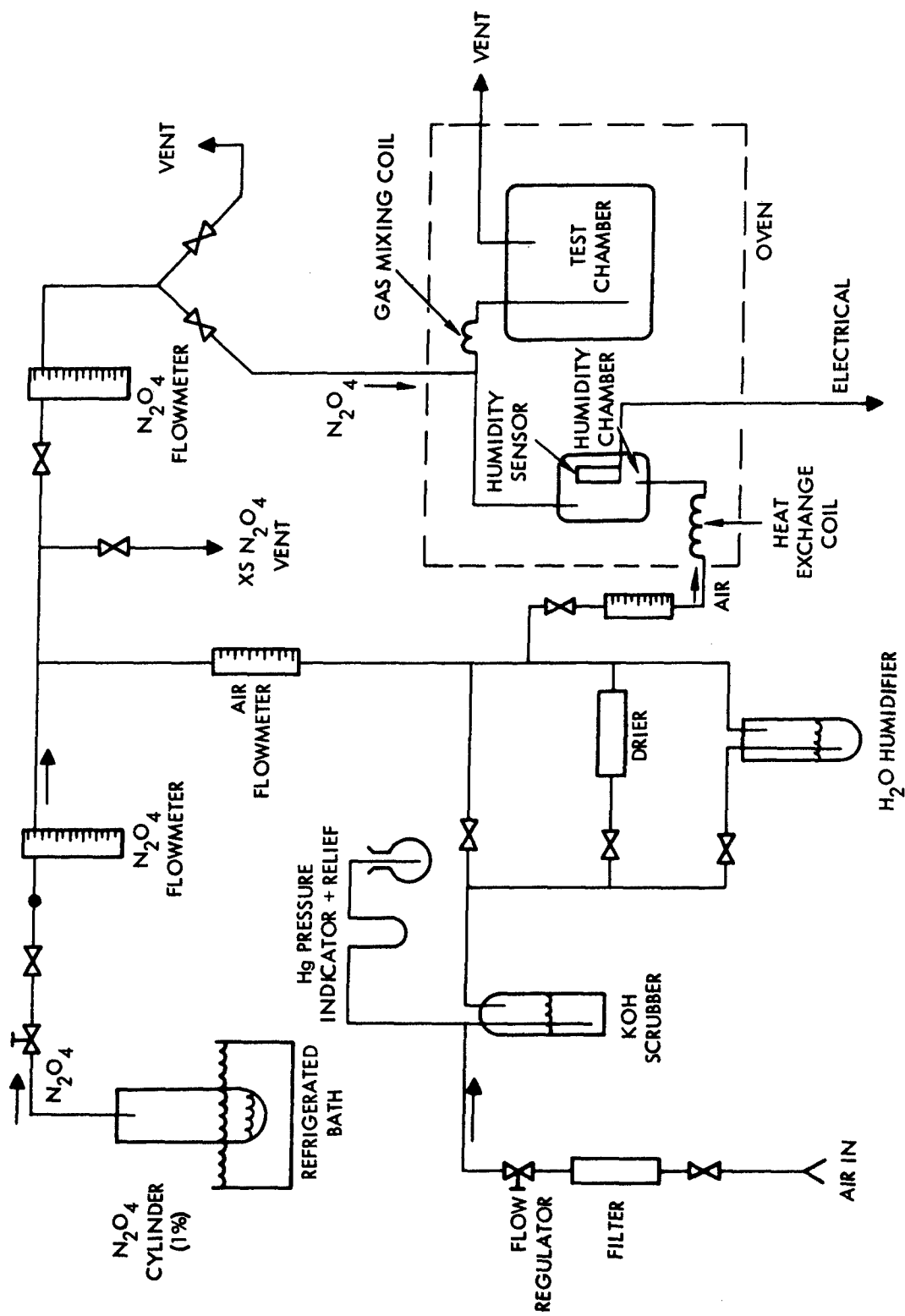


Figure 5. N₂O₄ Flow Apparatus

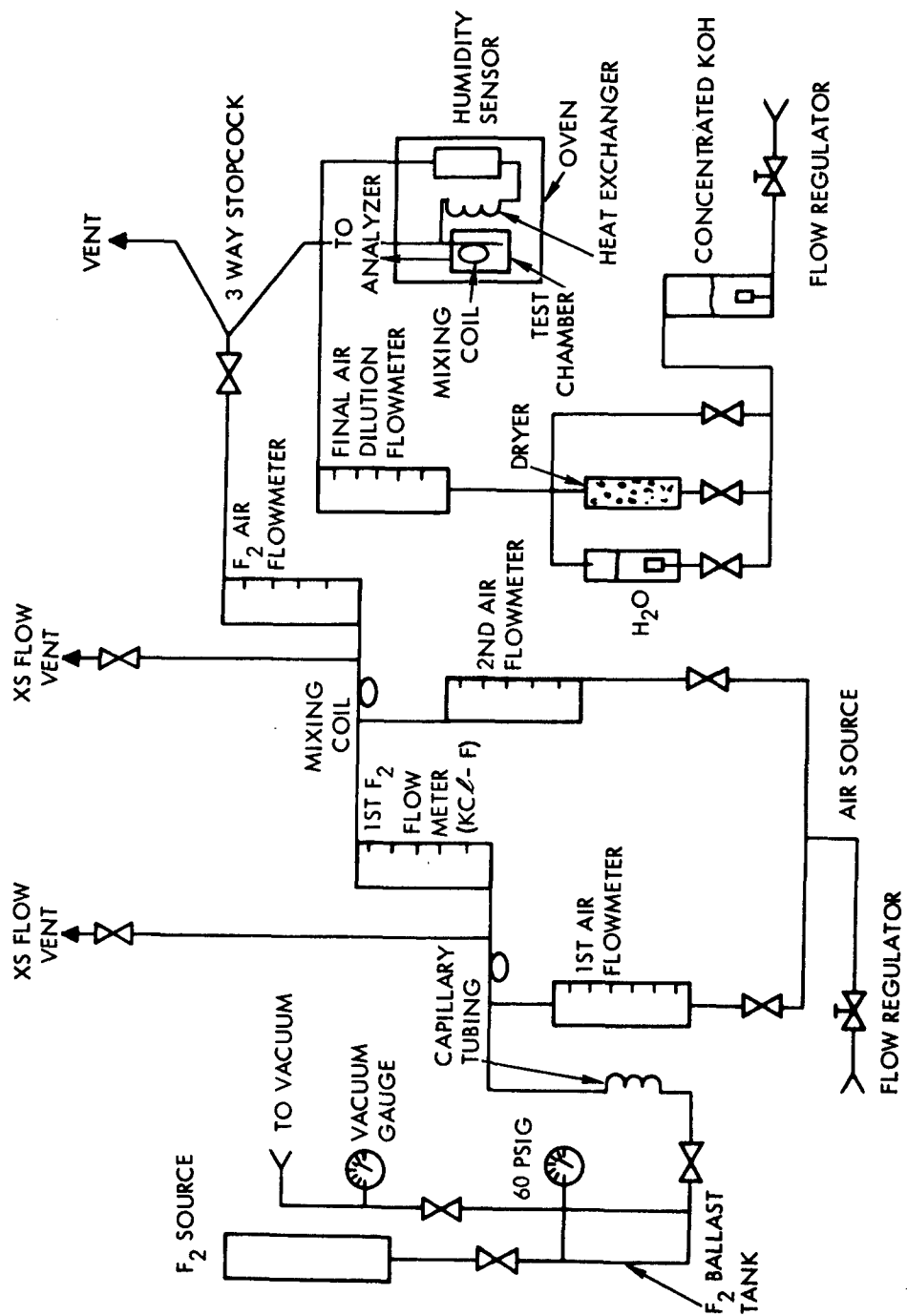


Figure 6. Fluorine Flow Apparatus

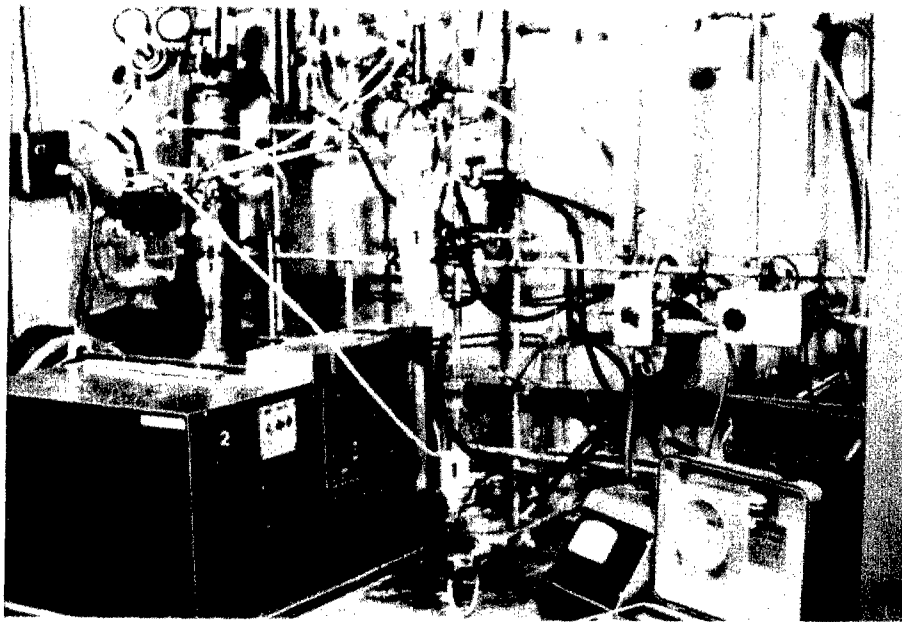


Figure 7. N_2O_4 Test Apparatus



Figure 8. N_2O_4 Test Chamber

Test air samples with known fluorine content were obtained by mixing pure fluorine and air. The pure fluorine flowed through a coil of stainless steel capillary tubing at approximately 0.3 ml/min, as measured by the flowmeter shown in figure 6. The rate was controlled by the pressure at the source tank. The fluorine was then diluted with air flowing at a rate that delivered the proper fluorine concentration to the chamber.

An MSA analyzer, shown in figure 9, was used to check the concentrations of the gases as they left the chamber. At required flow rates of the diluted fluorine in the range of 2 to 6 l/min, corresponding to a linear velocity of 20 to 60 cm/min, the amount of fluorine consumed in reacting with the sensors was insignificant. Standard concentrations of gas used for calibrating the MSA analyzer were prepared by using an electro-mechanical syringe feed system to inject known flows of gas mixtures into the analyzer gas stream. Both the feed syringe and MSA analyzer flowmeter were calibrated beforehand.

TEMPERATURE AND HUMIDITY CONTROL

Humidity

The apparatus for controlling the air humidity can be seen in figure 7. The air was first bubbled through a KOH solution to remove contaminants, then through a drying unit or a water bubbler or a bypass. By controlling the rates at which it flowed through these units with flow valves, any relative humidity from 0 to 100 percent could be obtained. An electronic hygrometer (HygroDynamics, Inc.), shown in figure 10, was used to determine the relative humidity. This humidity detector was placed immediately before the test chamber.

Temperature

Early tests in this program were conducted at room temperature, or approximately $22 \pm 2^{\circ}\text{C}$. For the tests in which the effect of temperature on reaction rates was measured, the test chamber and humidity sensing element, along with a length of copper tube through which the incoming air passes, were placed in either a thermostatically controlled oven or a cold bath (shown in figure 7), which controlled the temperature to $\pm 0.5^{\circ}\text{C}$. The relative humidity was always measured at the test temperature.

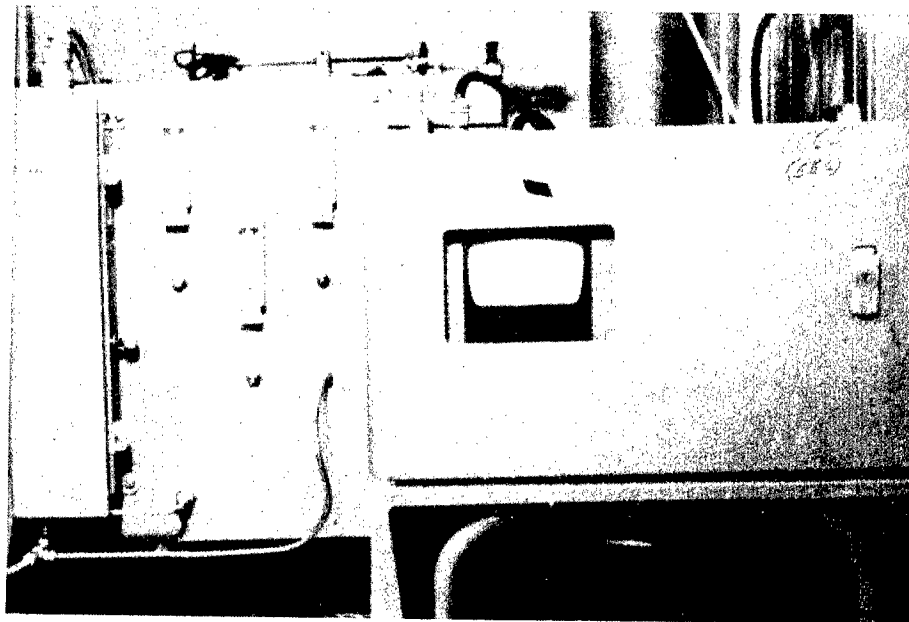


Figure 9. MSA Vapor Analyzer

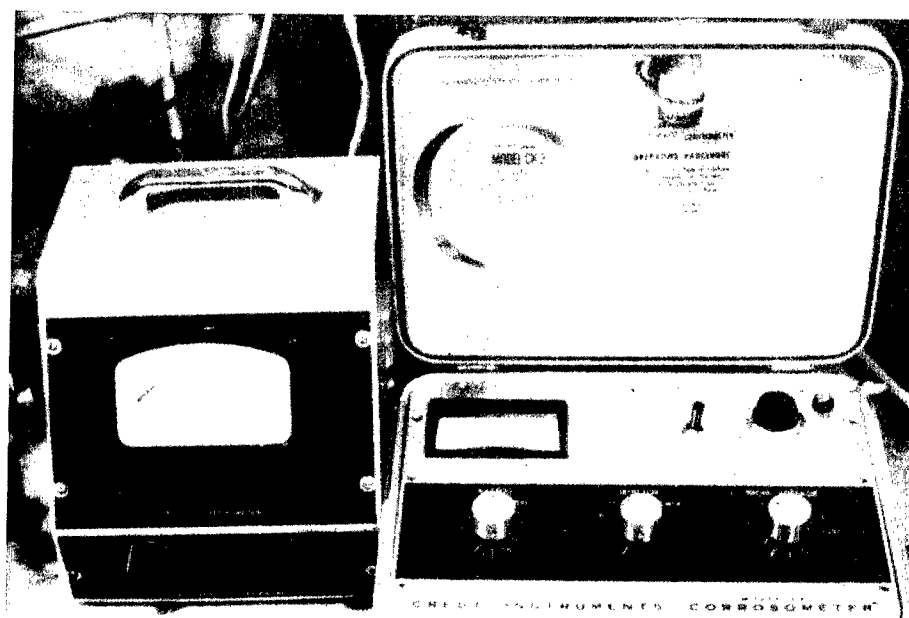


Figure 10. Humidity Indicator and "Corrosometer"

SECTION III

RESULTS AND DISCUSSION

SENSOR STABILITY AND REPRODUCIBILITY

The factors that might have a direct effect on reproducibility were studied to determine what steps could be taken to improve the uniformity of response. The factors studied included film thickness, method of sensitizer application, and the means of handling and storing films.

Film Thickness

A series of experiments were conducted in which films were grouped according to their initial resistance. The average resistance of the matched groups ranged from 55 to 85 ohms. In previous research by this corporation,* we used the "Corrosometer" to measure the change in resistance of the films after exposure to 10 ppm N_2O_4 (70°F, 50 percent R. H.). When the "Corrosometer" dial readings were used directly, the average deviation of the results was approximately 40 percent. However, when the results were corrected for initial resistance by using equation 7, the calculated exposure factor had a standard deviation of only ± 20 percent.

Four additional experiments were conducted with films of four widely different resistances, exposed concurrently, to obtain a direct comparison of the effect of the film resistance on the exposure factor. Figures 11, 12, and 13 show the exposure factor versus initial film resistance for 5, 10, and 15 minute exposures. These results show that in the range of initial resistance of 40 to 75 ohms, the exposure factor is relatively independent of the initial resistance. At low resistance values, however, there is a definite change in the exposure factor. This change may be explained by the differences in the crystal structure of the film which, in turn, will affect the kinetics of the reaction. The structure of the thinner films of higher resistance will be more influenced by the substrate upon which they are deposited.

*Thin Metal Film Detection System, AD 418 082, RTD-TDR-63-1079, Magna Corporation, Research and Development Division, Final Report for Contract AF04(611)-8501.

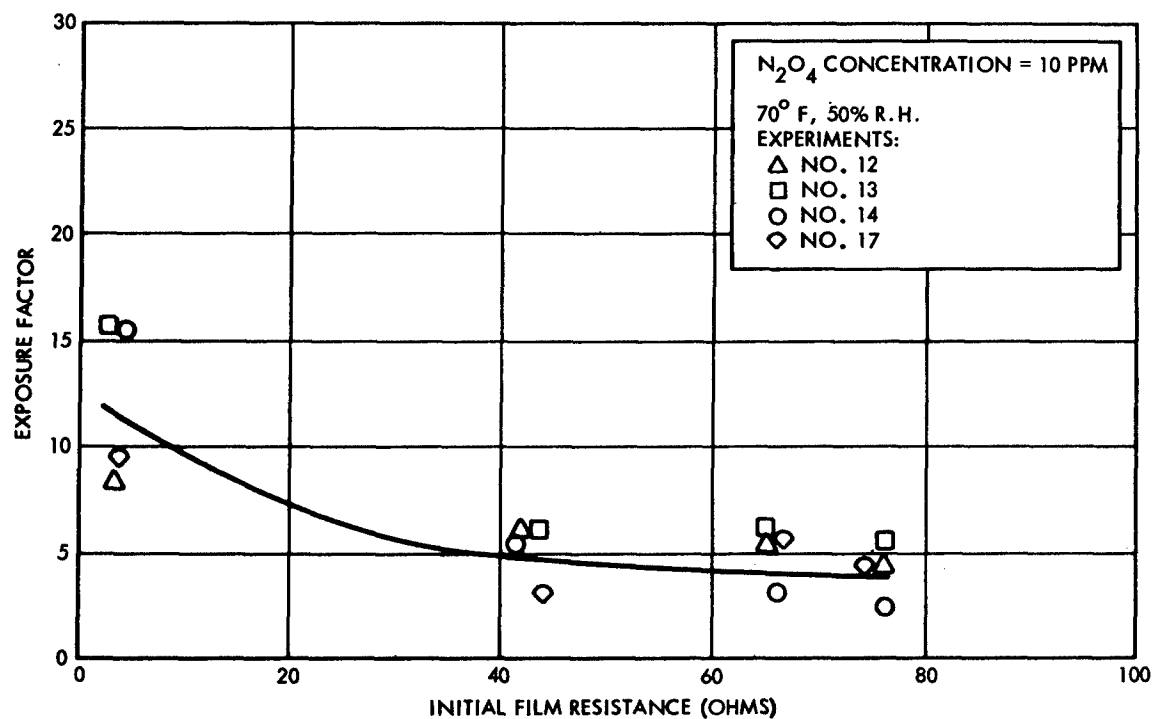


Figure 11. Exposure Factor versus Initial Film Resistance of Silver Films — 5 Minute Exposure

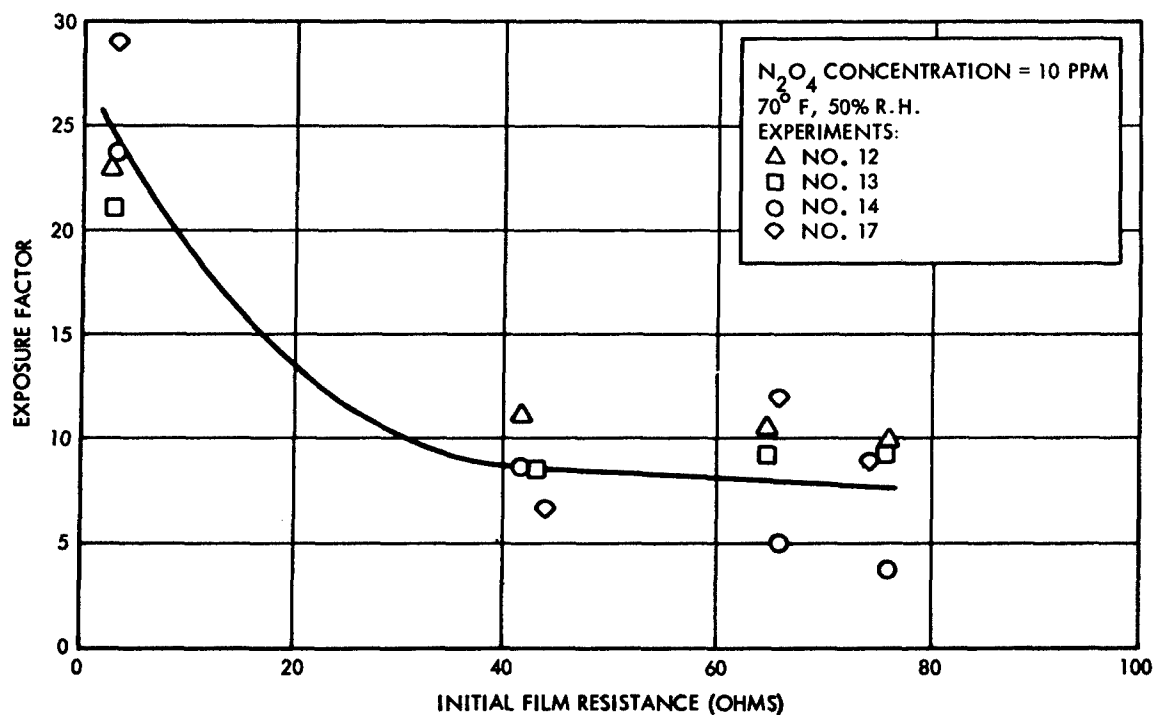


Figure 12. Exposure Factor versus Initial Film Resistance of Silver Films — 10 Minute Exposure

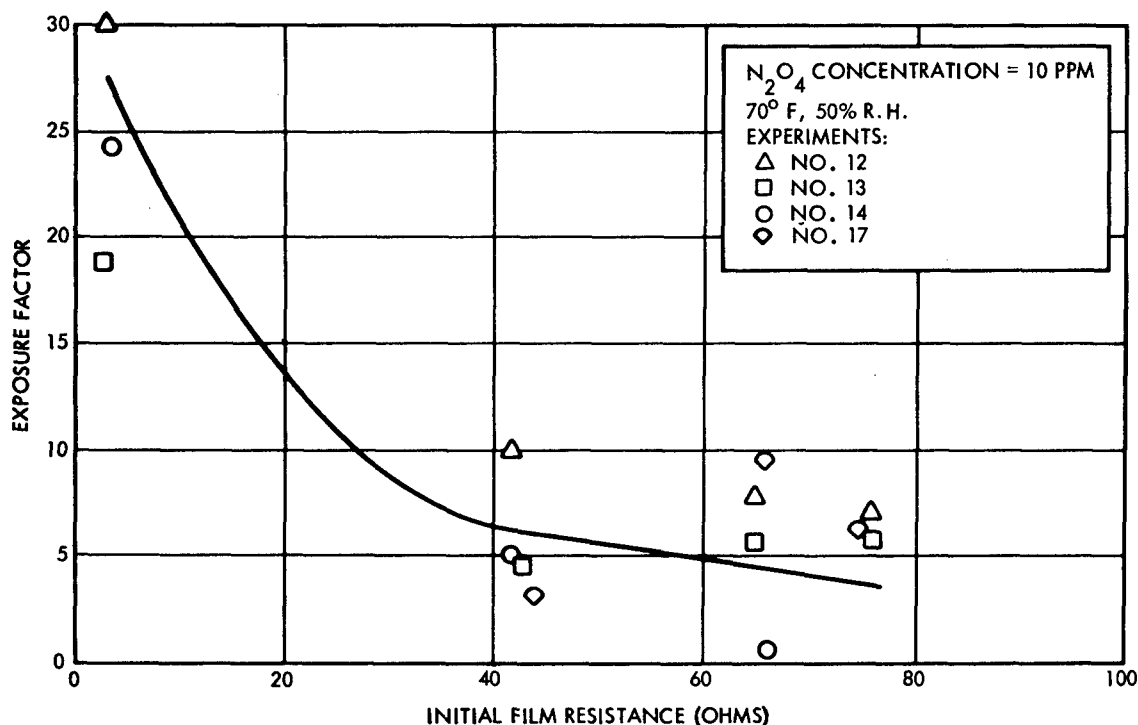


Figure 13. Exposure Factor versus Initial Film Resistance of Silver Films—15 Minute Exposure

Variations in the exposure factor at any given resistance on these curves can be a result of fluctuations in experimental conditions, variation in sensitizer application, or variations in the surface lattice structure of the metal film. For example, examination of substrate surfaces upon which the metal films are deposited has shown that the surface roughness varies considerably from one substrate to another. The effect of surface roughness of the substrate on response was determined by sandblasting some surfaces prior to deposition of the silver film. The sandblasted surfaces have lower and less reproducible responses than those that were not sandblasted. The surface condition of the substrates is, therefore, believed to be an important factor affecting reproducibility.

One source of variation in the initial resistance of the vacuum deposited silver films is the position of the substrate in the vacuum deposition chamber. For 90 percent of the films, the position in the vacuum deposition chamber had no significant effect on the initial film resistance; however, for about 10 percent of the films, the average resistance was 60 percent higher than the mean (table I). However, films with similar initial resistances behaved similarly regardless of their location in the chamber.

Table I. Film Resistance Variation with Position in Vacuum Deposition Chamber

Group	Position in Chamber (distance from center, inches)	Average Resistance (ohms)	Mean Resistance of Group (ohms)
I	1	35	32
	2 to 2-1/2	34	
	3 to 3-1/2	27	
	4 to 4-1/2	31	
	5	27	
	6	35	
	7 to 7-1/2	37	
II	8	52	53
	9	53	

To establish more clearly the role of the initial resistance, two separate groups of films with matched but different initial resistances were prepared (table II). Group I was selected so that the initial resistance was 45 ± 2 ohms, and Group II was selected so that the average initial resistance was 31 ± 2 ohms. Statistical tests of the reproducibility of the exposure factor to 10 ppm N_2O_4 showed standard deviations of 16 percent and 7.4 percent respectively for the two groups. However, the standard deviation of all eight samples from the two groups under the same conditions was 37.4 percent, as shown in table II, thus clearly establishing the important effect of initial resistance on reproducibility. The initial resistance is a function of both the film thickness and surface roughness; therefore the control of these factors is a major factor in the control of sensor reproducibility.

Sensitizer Application

Initially, the sensitizer salts were applied by dipping the films in aqueous solutions of the salts, following which the films were air dried. This resulted in uneven drying, leaving spots or rings of uneven salt deposits on the films that became visible after exposure to N_2O_4 . Three

alternative methods of applying the salt were examined: (1) dipping the film in the salt solution, then flash drying it with a heat gun, (2) spraying a controlled amount of solution onto the film with an air brush, and (3) spreading a controlled thickness of solution made viscous by means of a gel.

Table II. Reproducibility of Exposure Factor to 10 PPM of N_2O_4 of Films Sensitized with 0.1 Percent KCl in MeOH (1 percent H_2O)

Experiment	Sample Number	Exposure Factor at 10 Minutes	Deviation from Mean (percent)
No. 38	1	6.9	4.5
	2 45-ohm films	5.3	20
	3	6.5	1.5
	4	7.8	18
		Avg: 6.6	Std. Dev: 16
No. 33	1	10.7	6.1
	2 31-ohm films	10.8	5.3
	3	12.5	9.6
	4	11.7	2.6
		Avg: 11.4	Std. Dev: 7.4
All eight samples		Avg: 9.0	Std. Dev: 37.4

Standard deviation values were calculated using the following equation:

$$S = \sqrt{\frac{\sum d^2}{n-1}}$$

The first method, that of dipping and flash drying, formed the most uniform appearing surface and produced the most sensitive films (see table III). Further, this method proved to be the most convenient to use in sensitizing large quantities of films. The substitution of methanol (MeOH) for water as the solvent further improved this method. As shown in figure 14, this resulted in a considerable increase in sensitivity. This increase in sensitivity is believed to be due to the formation of smaller, more evenly distributed salt crystals on the film when methanol is used as the solvent.

Table III. Variation of Resistance Change with Different Sensitizing Methods

Sensitizing Method	Average Total Resistance Change in 10-Minute Exposure to 10 PPM N_2O_4 (percent)
Dipping and flash drying	50
Spraying	37
Gelled layer	33

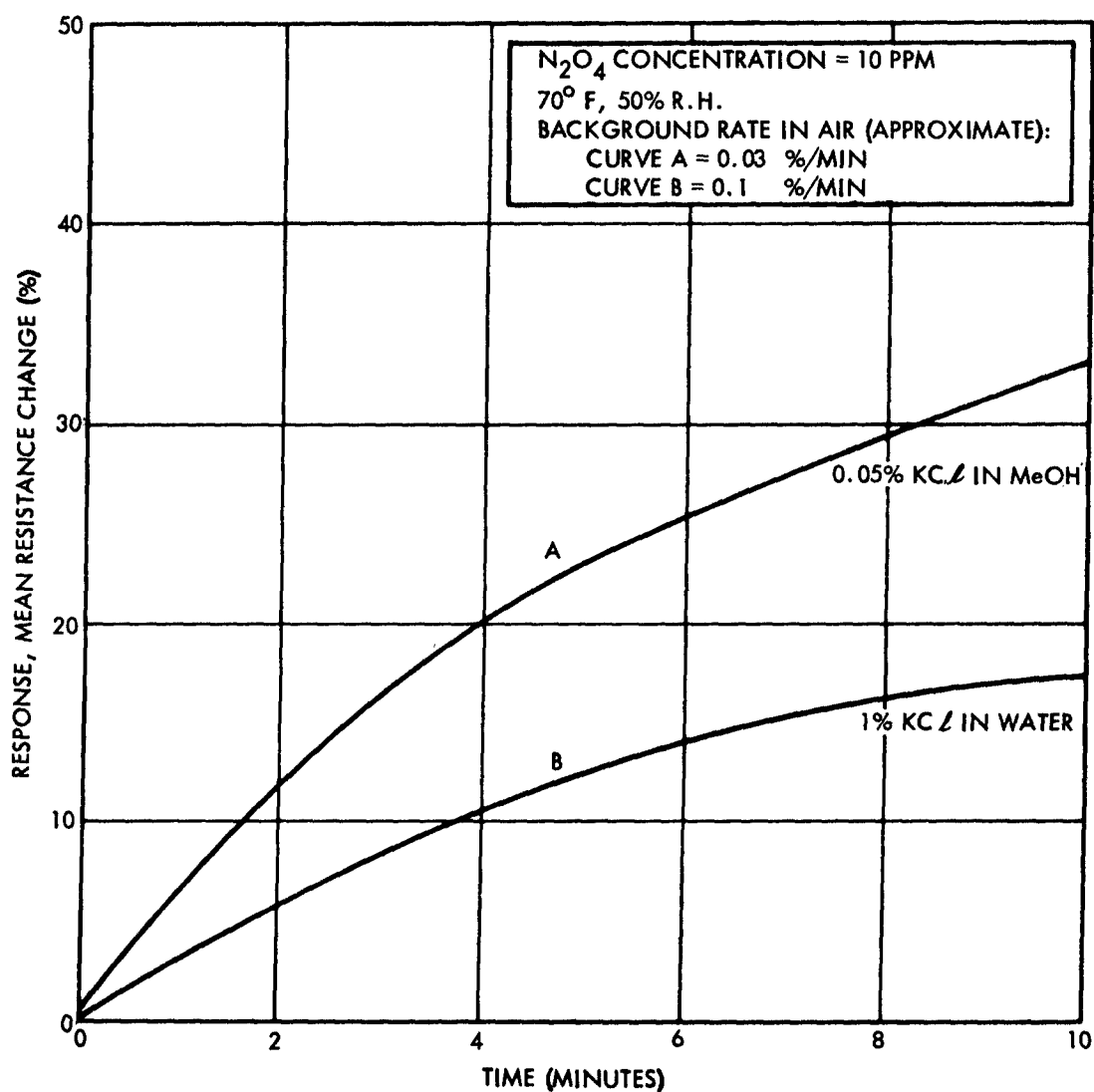


Figure 14. Effect of Sensitization Method on Response of Silver Films

Effect of Time on Sensitivity

The effect of time on the sensitivity of films to N_2O_4 was determined under conditions of ambient air exposure. Groups of four films each were sensitized and allowed to stand in normal laboratory air for various periods of time. At the end of each period a group of four sensors was exposed to 10 ppm N_2O_4 at 70°F and 50 percent R.H. Response data from three experiments covering a range of time intervals are given in table IV. The percentage loss in N_2O_4 sensitivity is given for each increment of air exposure. The data indicate only 27 percent loss in sensitivity after 4 hours air exposure and 50 percent loss after 24 hours. Even after 9 days exposure to air, 22 percent of the initial sensitivity was retained.

Although the sensitivity to N_2O_4 is reduced on prolonged exposure to air, the sensitivity loss during an 8 hour period is low enough to allow operation of the readout instrument. The original sensitivity of the film can be increased to give the desired response after a few hours exposure to air. Pre-exposure to air for a fixed time during manufacture may provide a more stable sensor by allowing the greatest part of the sensitivity loss to occur under controlled conditions prior to calibration of the sensors.

The effect of storage time on film sensitivity was also determined for films stored in a dessicator under air. The films were sensitized and stored in an ordinary laboratory dessicator until tested. The response of these films to 10 ppm N_2O_4 was determined after storage periods of 0, 38, and 70 days. The results as shown in table V, indicate that films stored in a desiccator for 38 days retained 42 percent of the initial sensitivity, while films stored for 70 days retained 22 percent of the initial sensitivity. This loss in sensitivity suggests that some other form of storage, such as storage under an inert gas, should be considered if the sensors are not used shortly after application of the sensitizer.

N_2O_4 SENSOR DEVELOPMENT

At the start of this program the N_2O_4 sensor was in the most advanced state of development of the three vapor sensors being investigated. The optimum metal-film, chemical-coating combination for the N_2O_4 sensor was already known—silver coated with KCl . Therefore, the development

Table IV. Effect of Exposure to Ambient Air on N₂O₄ Sensors

Experiment	Characteristic	Exposure to Ambient Air				
		0 Hours	1.5 Hours	4 Hours	24 Hours	27 Hours 9 Days
A	Mean exposure factor, 10-minute exposure to 10 ppm N ₂ O ₄ (70°F, 50 percent R.H.)	26		19	9.6	
	Standard deviation of samples	24%		16%	17%	
	Decrease in sensitivity	---		27%	50%	
						3.6
B	Mean exposure factor, 10-minute exposure to 10 ppm N ₂ O ₄ (70°F, 50 percent R.H.)	6.6				
	Standard deviation of samples	50%				30%
	Decrease in sensitivity	---				55%
C	Mean exposure factor, 10-minute exposure to 10 ppm N ₂ O ₄ (70°F, 50 percent R.H.)		18			4
	Standard deviation of samples		43%			48%
	Decrease in sensitivity	---				78%

effort dealt mostly with the evaluation of the effect of N_2O_4 concentration over the concentration range of 5 to 50 ppm and with a determination of the effect of humidity and temperature on the response.

Table V. Retention of Sensitivity of N_2O_4 Sensors During Storage in Desiccated Air

Characteristic	Duration of Storage of Sensors in Desiccator		
	0 Days	38 Days	70 Days
Mean exposure factor, 10-minute exposure to 10 ppm N_2O_4 (70°F, 50 percent R.H.)	11.4	4.8	2.5
Standard deviation of samples	6.9%	17%	35%
Sensitivity retained	---	42 %	22 %

The effect of N_2O_4 concentration at 70°F (21°C) and 50 percent R.H. on the response, calculated in units of exposure factor is shown in figure 15. Each point represents the mean of four samples. The percent standard deviation of individual samples from the mean was calculated for 10 minute exposure and the results were recorded on the figure. Note that the poorest reproducibility is 19 percent, and that any given time interval the response is nearly a linear function of N_2O_4 concentration.

The effect of relative humidity on the exposure factor at 70°F of films exposed to 5, 10 and 50 ppm N_2O_4 is shown in figures 16, 17, and 18 respectively. For the lower concentrations (5 and 10 ppm N_2O_4), the deviation caused by changes in relative humidity at any given time is less than 20 percent. At 50 ppm N_2O_4 , the relative humidity has a more dramatic effect, but in this case the critical performance zone is the first minute. Because of the high concentration of 50 ppm of N_2O_4 , the sensor would be asked to give an immediate alarm. From the appearance of the curves, during the first minute the effect of relative humidity is small. However, more careful analysis of the response during the first minute of exposure is required.

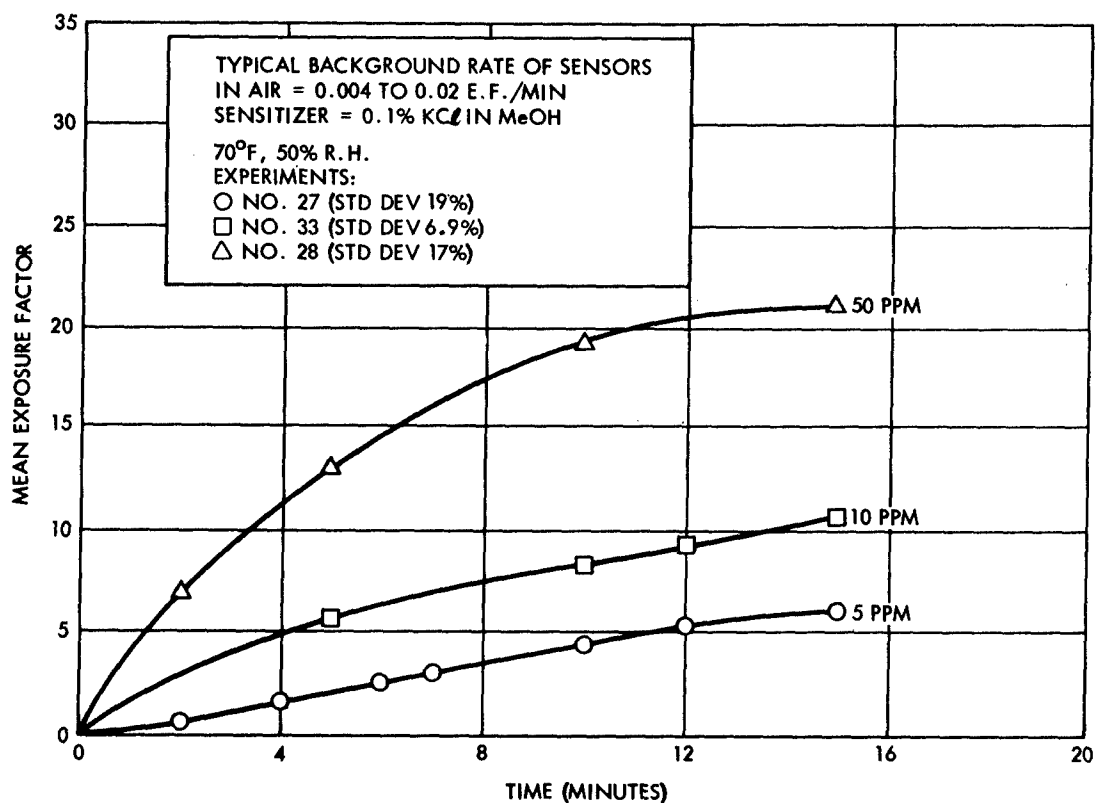


Figure 15. Effect of N_2O_4 Concentration on Exposure Factor of Silver Films

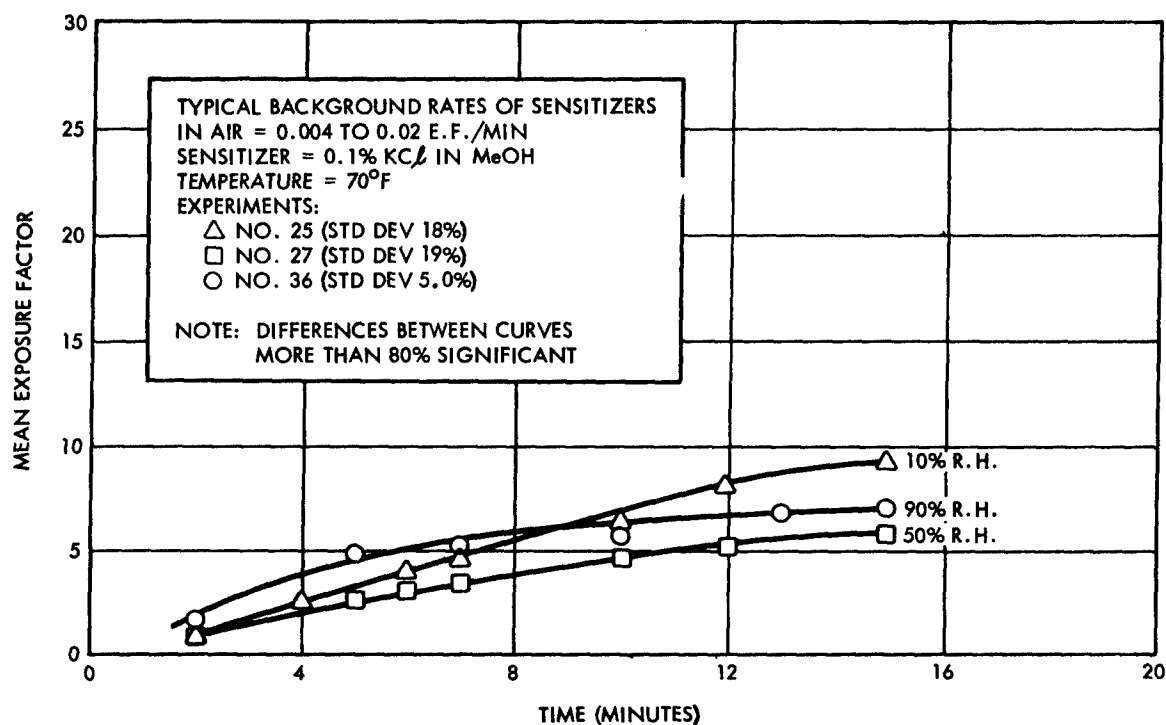


Figure 16. Effect of Relative Humidity on Exposure Factor of Silver Films (5 ppm N_2O_4)

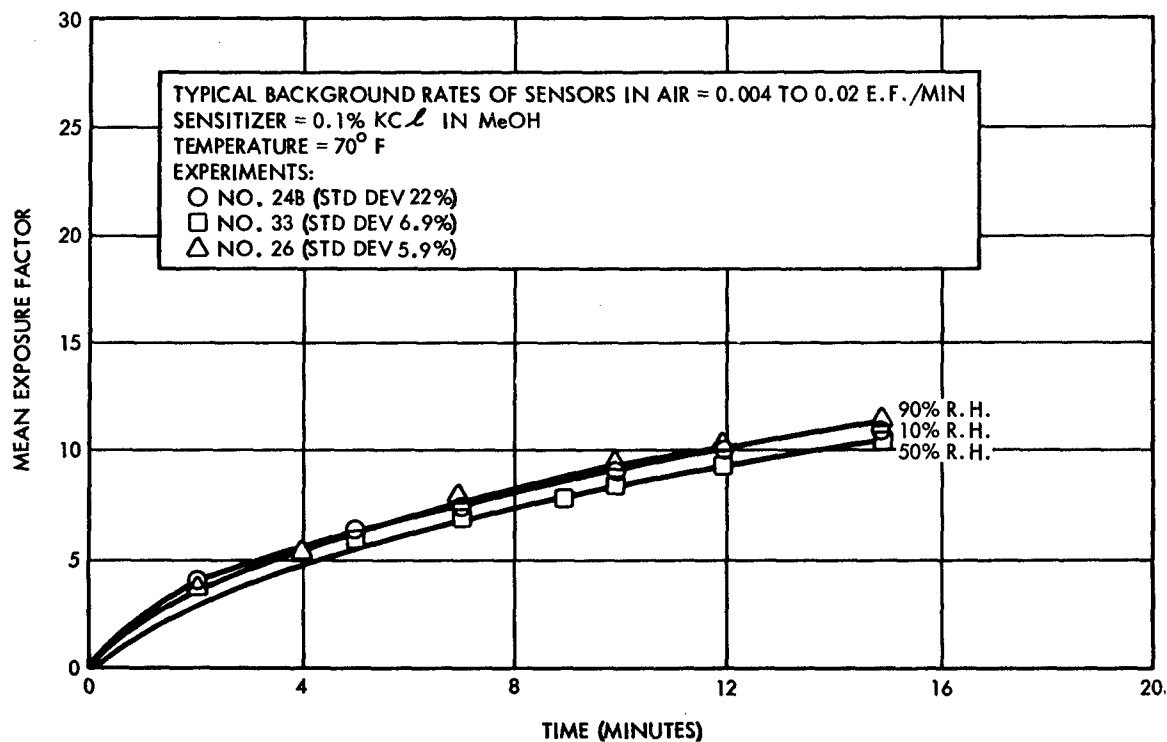


Figure 17. Effect of Relative Humidity on Exposure Factor of Silver Films (10 ppm N_2O_4)

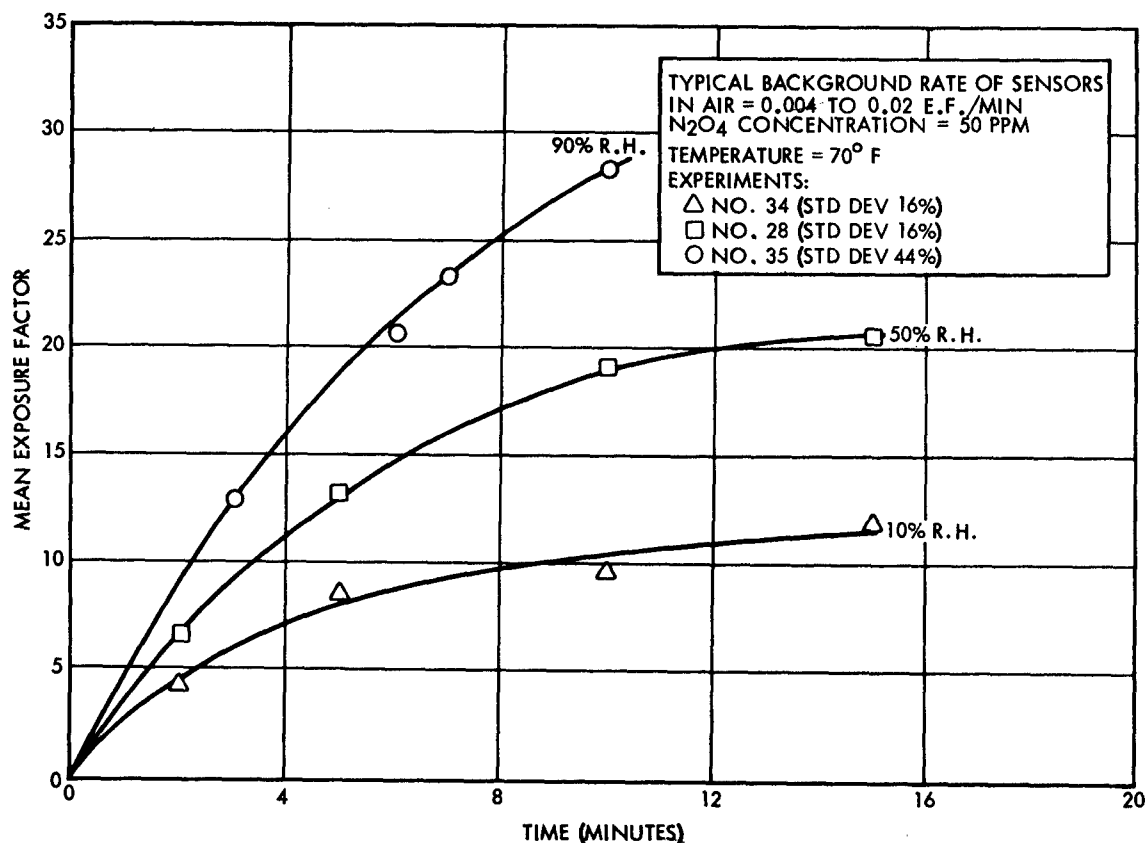


Figure 18. Effect of Relative Humidity on Exposure Factor of Silver Films (50 ppm N_2O_4)

The combined effect of temperature and humidity on the exposure factor to 10 ppm N_2O_4 is shown in figures 19 and 20 for temperatures of 50°, 70°, and 90°F, and humidities of 10 and 90 percent. The figures indicate that it would be difficult to compensate for the interaction of humidity and temperature; however, based on earlier results, if humidity or temperature were controlled, the effect of the other variable could be corrected by a fairly simple instrument-sensitivity control.

Several methods of maintaining an artificial humidity at the surface were investigated. The first approach involved enclosing the sensor in a small Lucite container, which was approximately 1/4-inch larger than the sensor in all dimensions. The container had an open window in front of the active sensor surface over which a thin membrane of Teflon was stretched. A cotton pad wetted with a saturated salt solution to give the desired humidity was placed in the bottom of the container. While this system successfully controlled the humidity, the diffusion of N_2O_4 through the membrane was too slow to give the desired sensitivity. A membrane more porous to the N_2O_4 is being sought.

Another means of reducing the effect of humidity involved the use of glycerol. When this material was added to the sensitizing solution a moist surface over a wide range of ambient humidities was formed. The addition of glycerol to the sensitizing solution reduced the effect of humidity on the response of N_2O_4 sensors from a 60 percent change in response between 10 percent and 50 percent R.H. to only 30 percent change. This method shows promise for use in reducing the effect of humidity to a point where it is not a significant problem.

An interesting sidelight to these studies is the fact that the exposure factor apparently goes through a minimum at 50 percent R.H. An examination of figures 16 and 17 shows the exposure factor at 50 percent R. H. to be less than the exposure factor at 10 percent or 90 percent. Although the difference is not large, it is statistically significant. This apparently anomalous behavior is not readily explained; however, it does suggest the possibility that there are two mechanisms by which N_2O_4 can attack the metal film, and that the preferred mechanism depends upon the availability of water.

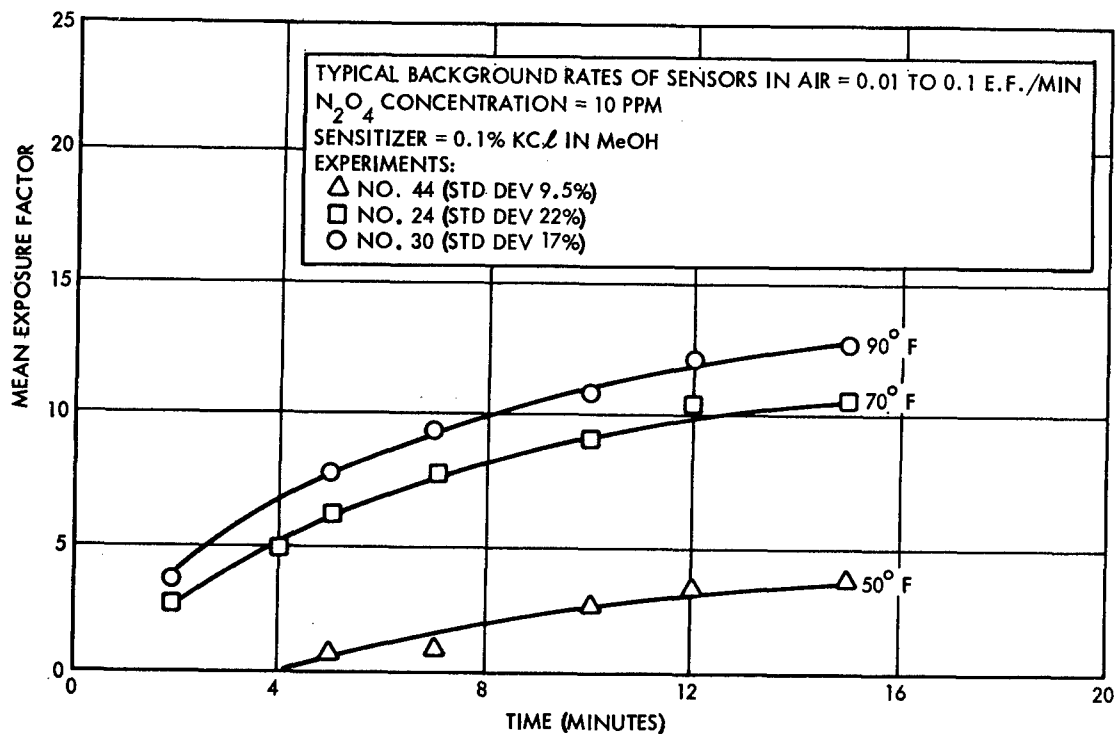


Figure 19. Effect of Temperature on Exposure Factor of Silver Films at 10 Percent R.H.

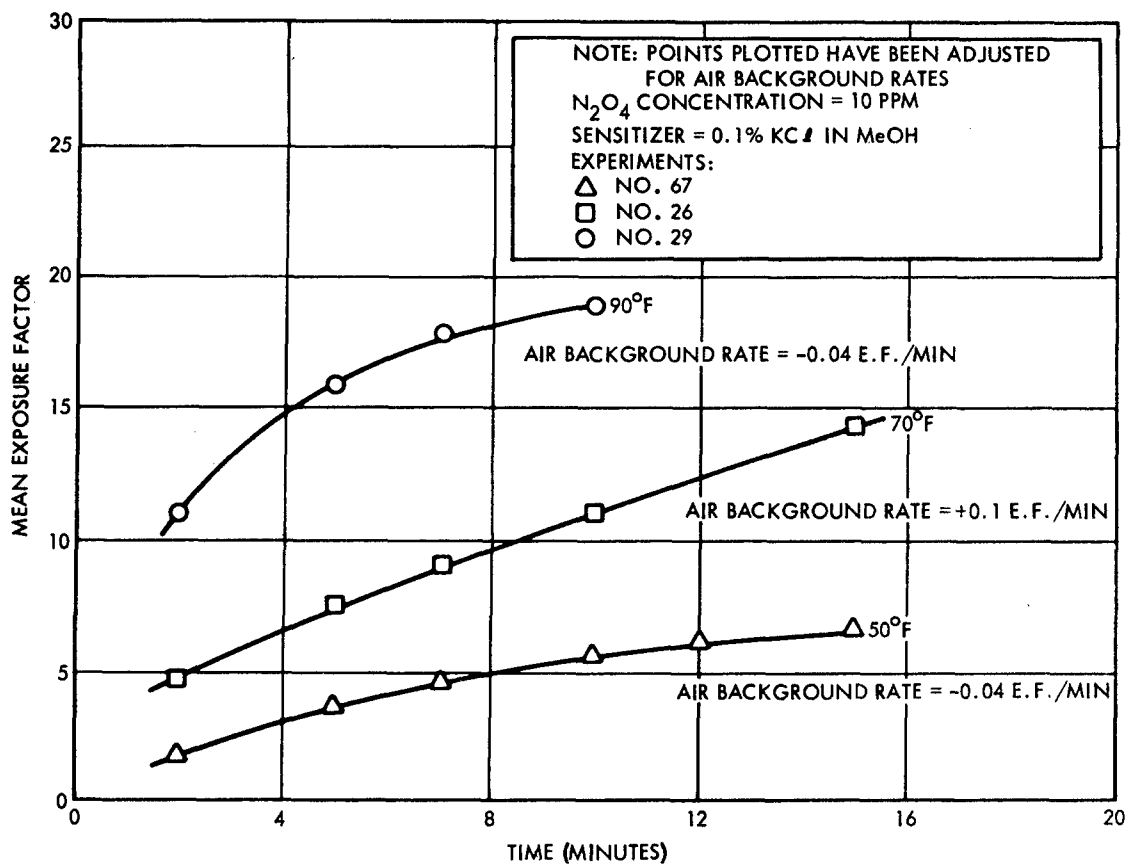


Figure 20. Effect of Temperature on Exposure Factor of Silver Films at 90 Percent R.H.

One reaction mechanism may be the direct oxidation of the metal by the vapor, while the other may involve either the absorption of the vapor in an absorbed moisture layer, with subsequent acid attack of the metal, or a combination of the vapor with atmospheric moisture, which then attacks the metal as an acid vapor, or a combination of these. Thus an acid attack could be occurring at high humidities and a direct oxidation at low humidities, with a combination of the mechanisms occurring at intermediate humidities. The direct oxidation is probably inhibited by a layer of water on the surface, while the acid attack is inhibited by saturation of the water layer with reaction products. Thus, at 50 percent humidity, where there is an adsorbed water layer, direct oxidation is inhibited, but because the amount of water available is limited, the water layer may be easily saturated and thus there is a minimum.

FLUORINE SENSOR DEVELOPMENT

Earlier experiments indicated that silver films coated with KCl or KBr could be used for fluorine detection,⁽¹⁾ but not with the required sensitivity. Various methods of improving the sensitivity were investigated. The effects of film resistance, concentration of the sensitizer solution, and method of application of the sensitizer on sensitivity and reproducibility were studied, using silver films sensitized with KCl. The best sensitivity, as shown in table VI and figures 21 and 22, was obtained with high-resistance films treated with a 2 percent KCl in MeOH solution. Other sensitizers examined were KBr, KOH, and a KCl-NH₄Cl mixture. The results, as shown in figure 23, were not significantly better.

* Thin Metal Film Detection System, AD 418 082, RTD-TDR-63-1079, Magna Corporation, Research and Development Division, Final Report for Contract AF04(611)-8501.

Table VI. Effect of F₂ Concentration on Silver Films

Film	Time (minutes)	Concentration of F ₂ (ppm)	Mean Exposure Factor	Mean Change in Resistance (percent)
200-ohm film sensitized with 1 percent KCl in MeOH dip (70°F, 50 percent R. H.)	5	1	0.05	1
		2	0.25	6
		15	2.2	38
	10	1	0.12	3
		2	0.52	12
	15	1	0.26	5.5
170-ohm film sensitized with 2 percent KCl in MeOH dip (70°F, 50 percent R. H.)	5	1	0.00	0.0
		2	0.08	0.9
	10	1	0.00	0.0
		2	0.15	1.4
	15	1	0.04	0.8
		2	0.24	2.5
105-ohm film sensitized with 2 percent KCl in MeOH dip	5	1	0.03	0.2
		2	0.10	----
		10	0.87	7
	10	1	0.06	0.4
		2	0.22	1
		10	3.0	24
	15	1	0.12	0.6
		2	0.37	2
		10	6.0	48

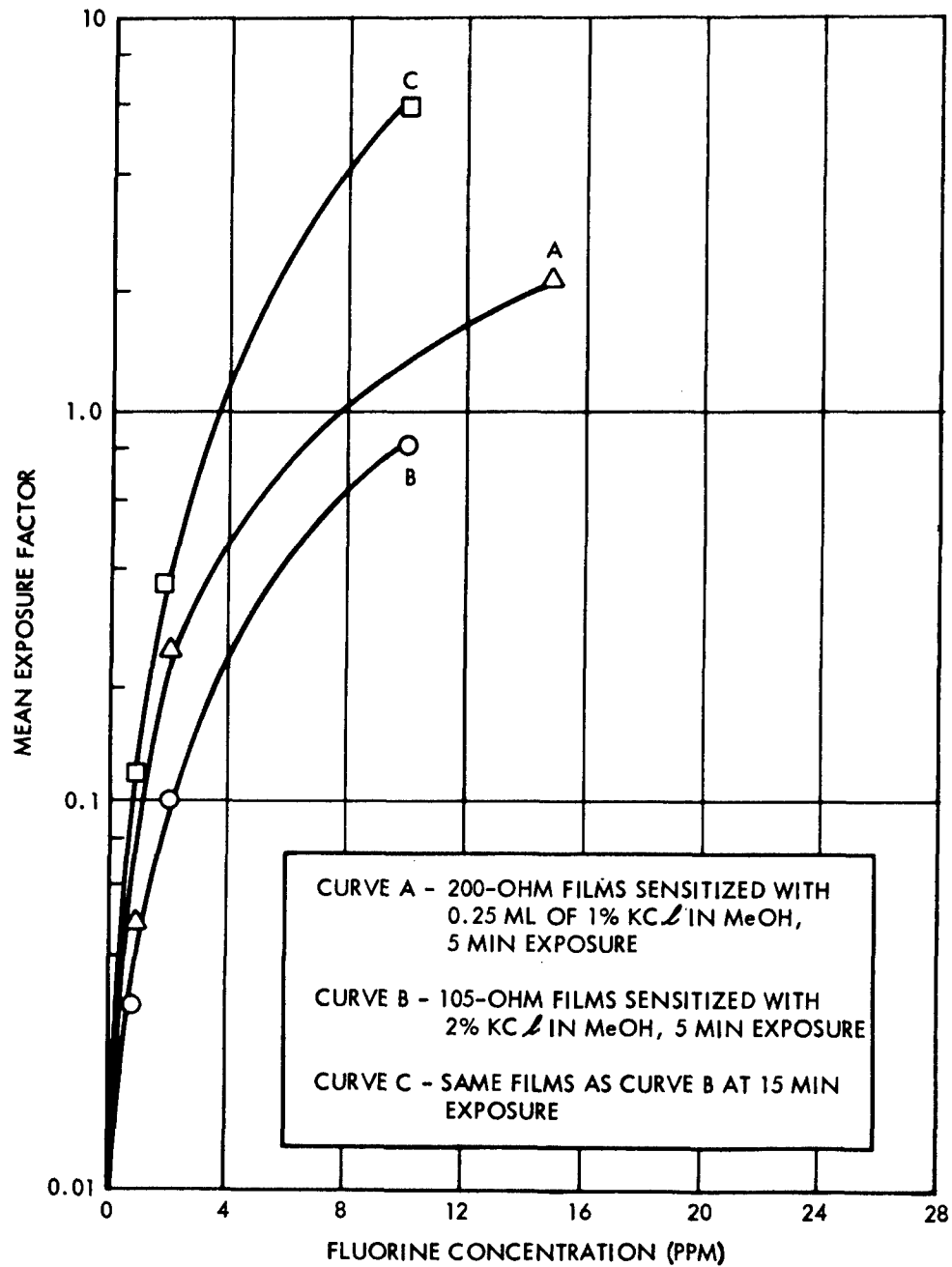


Figure 21. Exposure Factor of Silver Films versus Fluorine Concentration

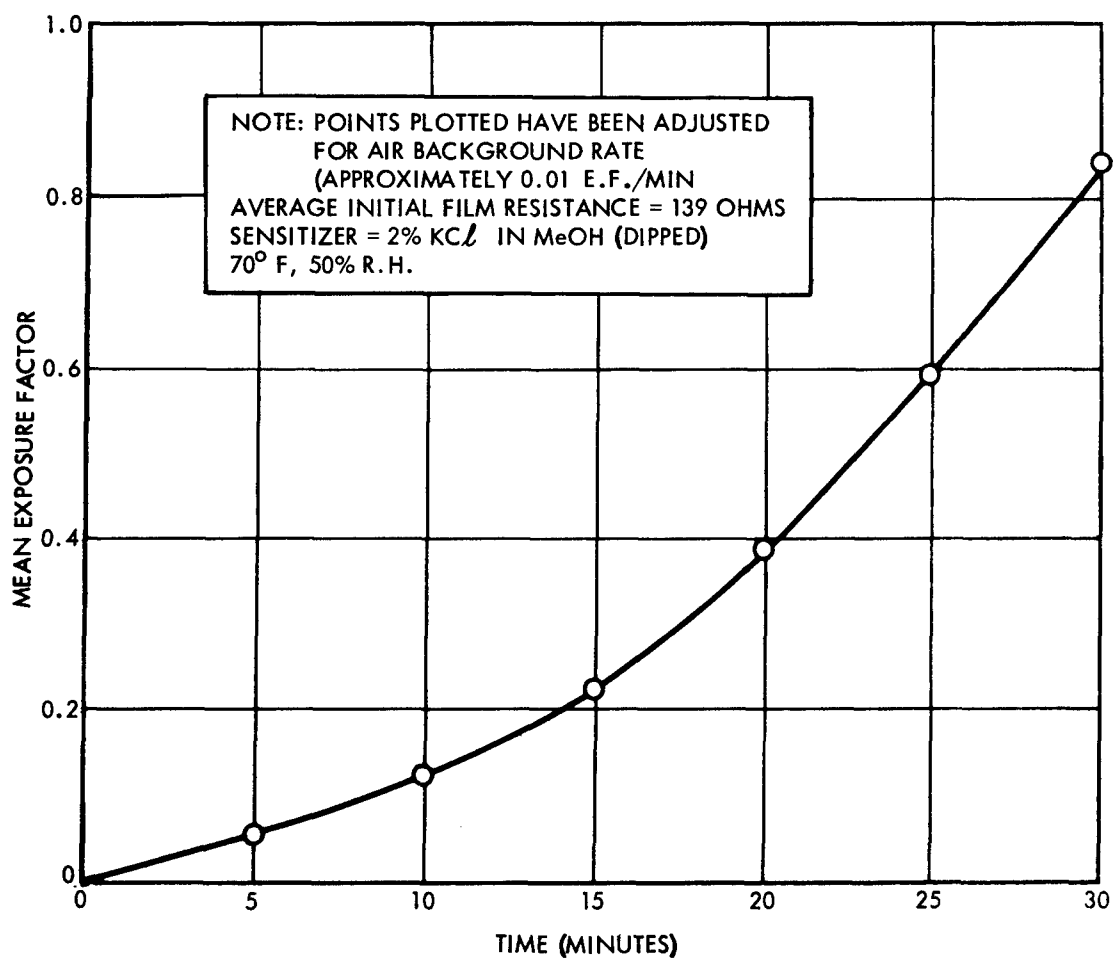


Figure 22. Exposure Factor of Silver Films in Response to 2 PPM Fluorine

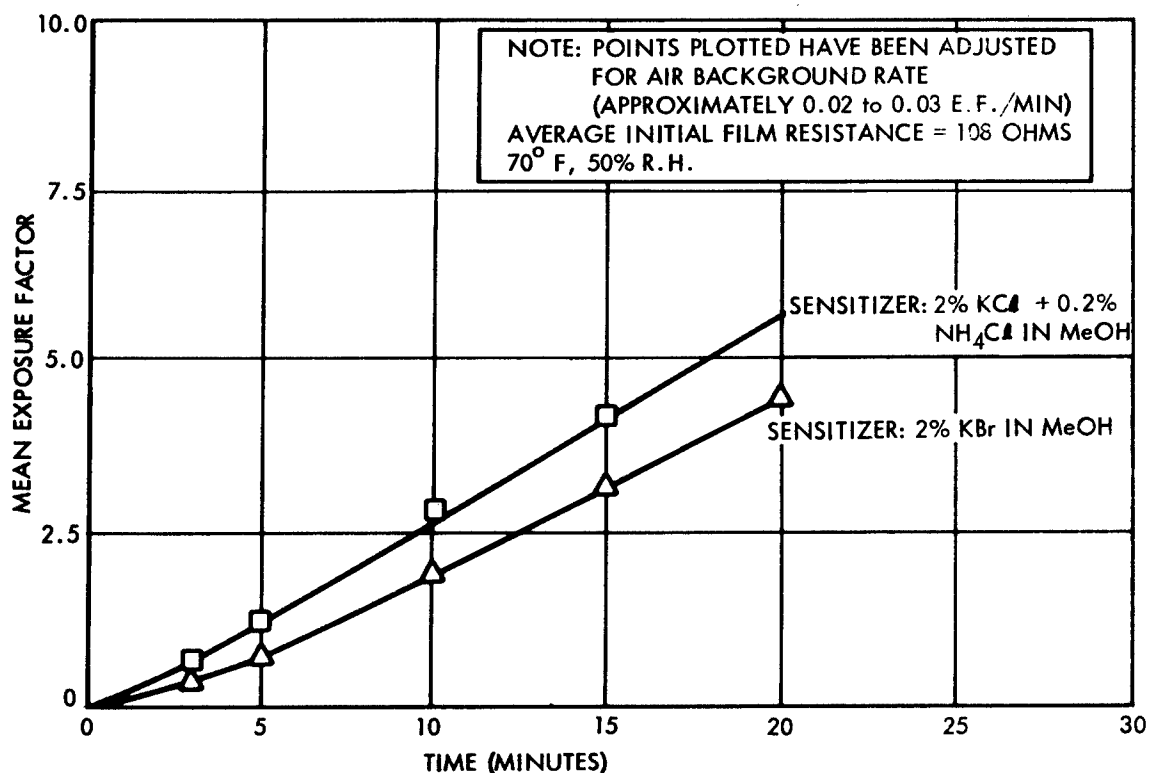


Figure 23. Exposure Factor of Silver Films in Response to 5 PPM Fluorine

Much more dramatic results were obtained when other metal films were substituted for the silver film. The results obtained with antimony, bismuth and copper films coated with KCl and KBr are summarized in tables VII and VIII, and the results for copper films are illustrated in figure 24. The best results were obtained with a copper film coated with KBr. The response at 5 ppm of fluorine was approximately one exposure factor per minute, which is four times the sensitivity of the best silver films tested. While the lower limit of fluorine concentration that can be detected with copper film sensors has not yet been specifically determined, a comparison of the response of 16-ohm copper films (table VIII) with that of silver films of much higher resistance (table VI) shows comparable sensitivities. Since the sensitivity is greatly dependent on film resistance, the use of higher-resistance copper films should provide significant response below one ppm, possibly as low as 0.1 ppm.

Table VII. Response of Antimony and Bismuth Films
to 5 PPM F_2

Film	Sensitizer	Time (minutes)	Exposure Factor	Change in Resistance (%)
500-ohm antimony	2% KCl in MeOH (30% H_2O)	20	0.0	0.0
900-ohm antimony	2% KBr in MeOH (20% H_2O)	5	0.03	4
		10	0.04	5
		20	0.05	7
2200-ohm bismuth	2% KCl in MeOH (30% H_2O)	20	0.0	Nil
2200-ohm bismuth	2% KBr in MeOH (20% H_2O)	10	0.00	0.2
		20	0.01	1.0

Table VIII. Response of Copper Films to 5 PPM F_2

Film	Sensitizer	Time (minutes)	Exposure Factor	Change in Resistance (%)
22-ohm copper	2% KOH in MeOH (0.5% H_2O)	3	0.6	
		5	0.7	3
		10	0.9	4
		20	1.4	6
26-ohm copper	1% $NH_4H_2PO_4$ in MeOH (25% H_2O)	20	0.0	0.0
14-ohm copper	2% KCl in MeOH (30% H_2O)	3	0.8	
		5	1.5	1.5
		10	4.0	4
		20	12	13
16-ohm copper	2% KBr in MeOH (20% H_2O)	3	1.7	6
		5	6.4	8
		10	11	15
		20	23	34

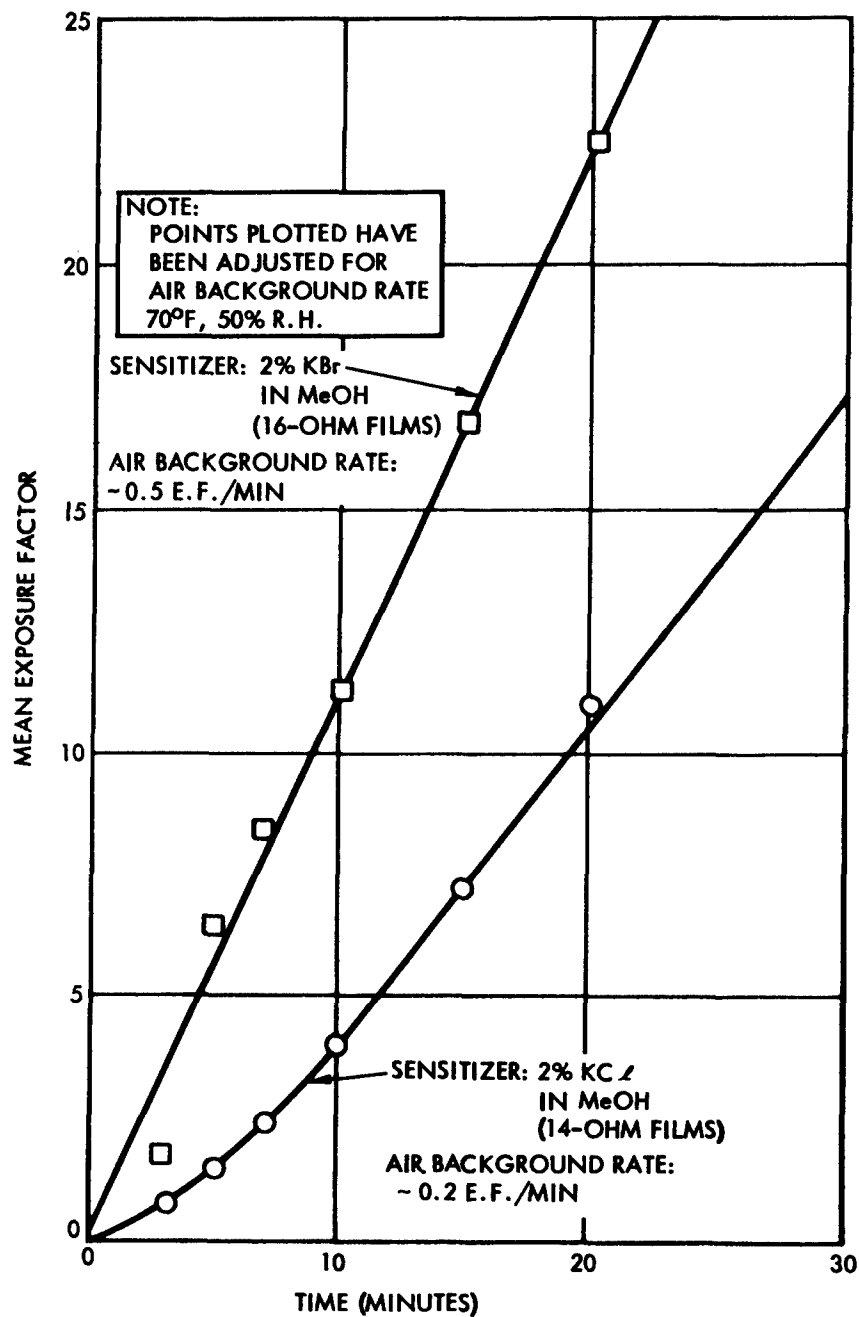


Figure 24. Exposure Factor of Copper Films in Response to 5 PPM Fluorine

The air oxidization rates of the silver and copper films, measured in clean air at 50 percent R.H., which are shown in table IX, are high initially but decrease with time. The copper films coated with KCl or KBr have the lowest air oxidization rates of any of the sensors that showed a high response to fluorine. The use of higher-resistance films to increase the lower limit of concentration that can be detected with copper films will cause some increase in air oxidation rates.

When temperature and humidity effects on the copper films were examined (figures 25 and 26), only a small effect was observed. Although the results presented in figures 25 and 26 cannot be compared directly with the exposure factor data in figure 24 because the initial resistances of the films are not the same, the effect of temperature and humidity should be the same percent of the response in each case.

Copper films coated with KBr, because of their potentially greater sensitivity at low concentrations and comparable air oxidation rates to silver films, were selected for use with the breadboard instrument for detecting fluorine. The lowest fluorine concentration tested with this combination was 5 ppm. Response of copper films to fluorine at concentrations of less than 1 ppm is predicted on the basis of results presented for silver films tested at 1 ppm.

UDMH SENSOR DEVELOPMENT

Fuels such as UDMH are strong reducing agents, as opposed to the strong oxidizing agents discussed previously. Therefore, the development of a UDMH sensor was approached from the viewpoint of forming a metallic film by reducing a metal salt deposited on a substrate. The resulting decrease in resistance would then be a measure of exposure to UDMH, in contrast to N_2O_4 and F_2 detection, which depended on oxidation of the metal.

Several combinations of metal films and salts were examined. Table X summarizes the results obtained when they were exposed to 1000 ppm of the fuel vapor. Data on UDMH were obtained before the adoption of the exposure factor method of reporting response, and the results are therefore shown as percent change in resistance; however, the relative sensitivities are the same, being independent of the method of reporting. Untreated films of Cu, Mg, Ni, Sr, Zn, Pb, Al, Sb, and Ge showed no significant

Table IX. Air Oxidation Rate of Films with Various Sensitizers

Sensitizer	Film Resistance (ohms)	Time (minutes)	Air Oxidation Rate (exposure factor/hour)
<u>Silver Films</u>			
2% KCl in MeOH (dipped)	110	60	0.97
	90 to 170	50	2.3
	140	75	0.85
	110	45	1.1
2% KCl + 0.2% NH ₄ Cl in MeOH	110	45	2.2
2% KOH in MeOH	110	45	0.11
2% KBr in MeOH	110	45	1.6
<u>Copper Films</u>			
2% KCl in MeOH	15	45	3.0
	15	110	0.72
2% KBr in MeOH	27	60	2.8
	27	110	2.0
		7 hr	1.4
	20	110	2.1
2% KOH	22	110	0.21
2% KOH	22	110	1.7

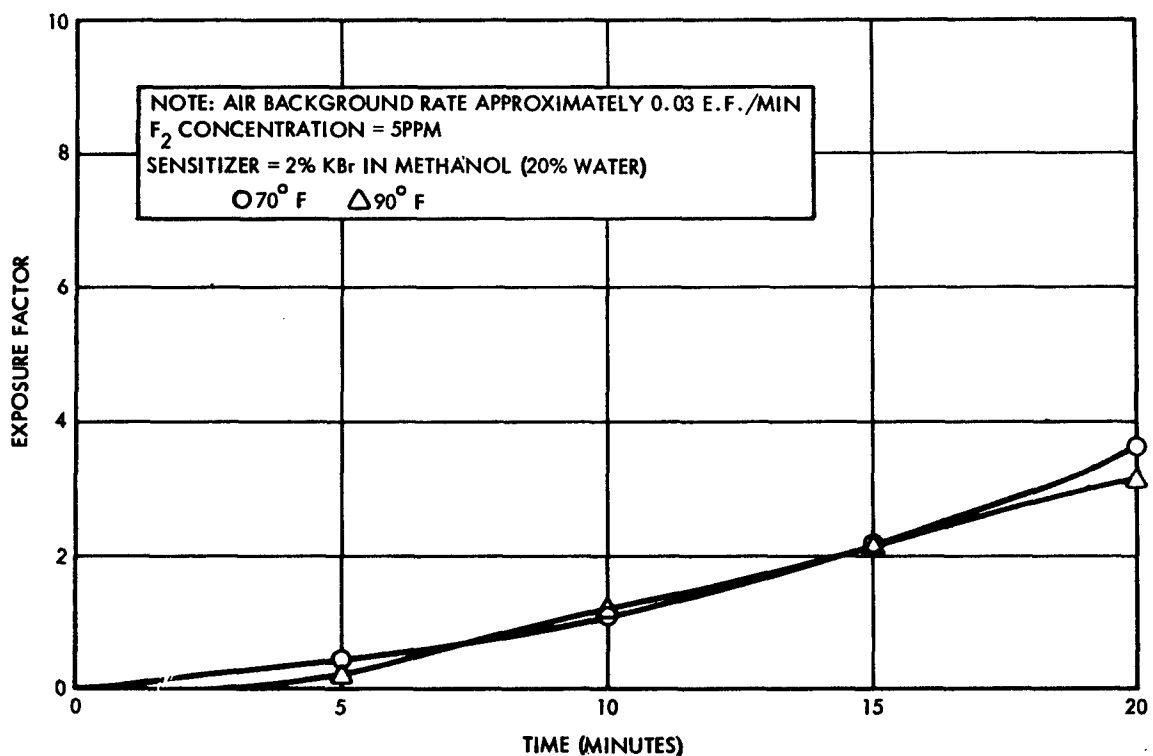


Figure 25. Effect of Temperature on Exposure Factor of Copper Films Exposed to 5 PPM Fluorine

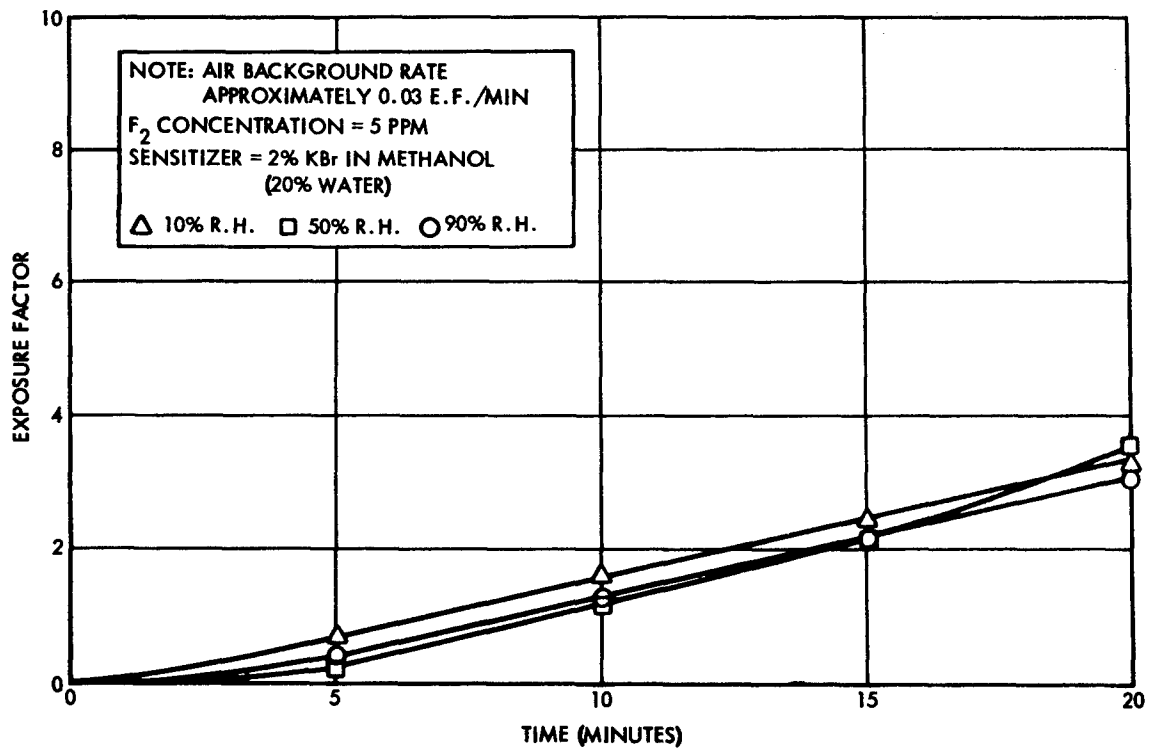


Figure 26. Effect of Relative Humidity on Exposure Factor of Copper Films Exposed to 5 PPM Fluorine

Table X. Response of Films to N_2H_4 /UDMH Vapor (1000 ppm)

Metal	Salt	Average Response (percent resistance change per minute)
Ag	AgNO_3	-3.1
Ag	LiClO_4	-2.4
Ag	$\text{Na}_2\text{S}_2\text{O}_5$	-0.40
Ag	Fe_2O_3	-0.23
Ag	HNO_3	-0.15
Ag	Na_2SO_3	-0.15
Ag	KI	+0.15
Ag	KOH	-0.10
Ag	H_2SO_4	-0.10
Ag	$\text{Cu}(\text{NO}_3)_2$	-0.05
Ag	NaNO_3	-0.05
Ag	$\text{Th}(\text{NO}_3)_3$	-0.05
Ag	CrO_3	-0.05
Ag	MnO_2	-0.05
Ag	KCl	None
Ag	I	None
Cu	H_2SO_4	+1.3
Cu	CuSO_4	+0.34
Cu	LiClO_4	+0.23
Cu	Na_2SO_4	None
Cu	$\text{Na}_2\text{P}_2\text{O}_7$	None
Cu	I	None

response, nor did Bi, Cu, Sn, and Sb films when coated with 1 percent HNO_3 and exposed to 100 ppm UDMH (table XI).

Table XI. Response of Sensitized Metal Films to UDMH (100 ppm)

Time	Total Resistance Change of Films (percent)			
	Bi	Cu	Sn	Sb
10 minutes	0.0	0.3	1.0	0.0
2 hours	0.9	9.9	3.3	0.0

Sensitizer: 1 percent HNO_3

Silver nitrate on silver was the first detection system found to have a sensitivity to UDMH. As a result, various other silver salt-metallic silver combinations were investigated. The results of these tests, presented in tables XII and XIII, and figures 27, 28, and 29 were encouraging. Silver acetate ($\text{AgC}_2\text{H}_3\text{O}_2$) on silver was the most sensitive system tested. The low results obtained at 1000 ppm are questionable because this test was conducted with a lower gas flow rate, in order to obtain the higher concentration, than was used for the lower concentrations. There is a question, therefore, as to whether adequate stirring of the air in the box was achieved with the low flow rates.

The effect of exposing the films to clean humidified (50 percent R.H.) air was determined for the silver films with various sensitizers (table XIV). During the first 24 hours the films underwent resistance changes of from 2 percent to over 10 percent, depending on the sensitizer used. After the first 24-hour period, the resistance became stable and any further changes due to background effects were insignificant. The response of the films to UDMH after the 24-hour aging in clean humid air (Table XV) was considerably lower than that of fresh films. The films with silver nitrate sensitizer were least affected by the aging process, the response to 100 ppm UDMH decreasing from resistance change rates of approximately 4 percent per minute to 1 percent per minute. The effect of aging on films with other sensitizers was greater, reducing the response to rates of 0.1 to 0.2 percent resistance change per minute at 100 ppm UDMH. However, the percent resistance change rates were much more consistent for films after the aging process than they are for fresh films.

Table XII. Response of Metallic Silver—Silver Salt Films to UDMH Vapor

Salt	UDMH (ppm)	Mean Response (percent resistance change per minute)
AgNO ₂	1000	-6.6
AgNO ₃	1000	-8.9
AgC ₂ H ₃ O ₂	1000	-2.9
AgNO ₂	100	-6.7
AgNO ₃	100	-4.3
AgC ₂ H ₃ O ₂	100	-9.0
AgNO ₂	10	-4.9
AgNO ₃	10	-1.5
AgC ₂ H ₃ O ₂	10	-6.2

Table XIII. Maximum Response Rates Obtained with Silver Films Exposed to 10 PPM UDMH

Sensitizer	Mean Maximum Response (percent change/min)	Time (minutes)
AgNO ₃ , 1 percent	1.5	5 to 7
AgC ₂ H ₃ O ₂ , 1 percent	6.2	1 to 2
AgNO ₂ , -AgOH, 1 percent	4.9	1 to 3

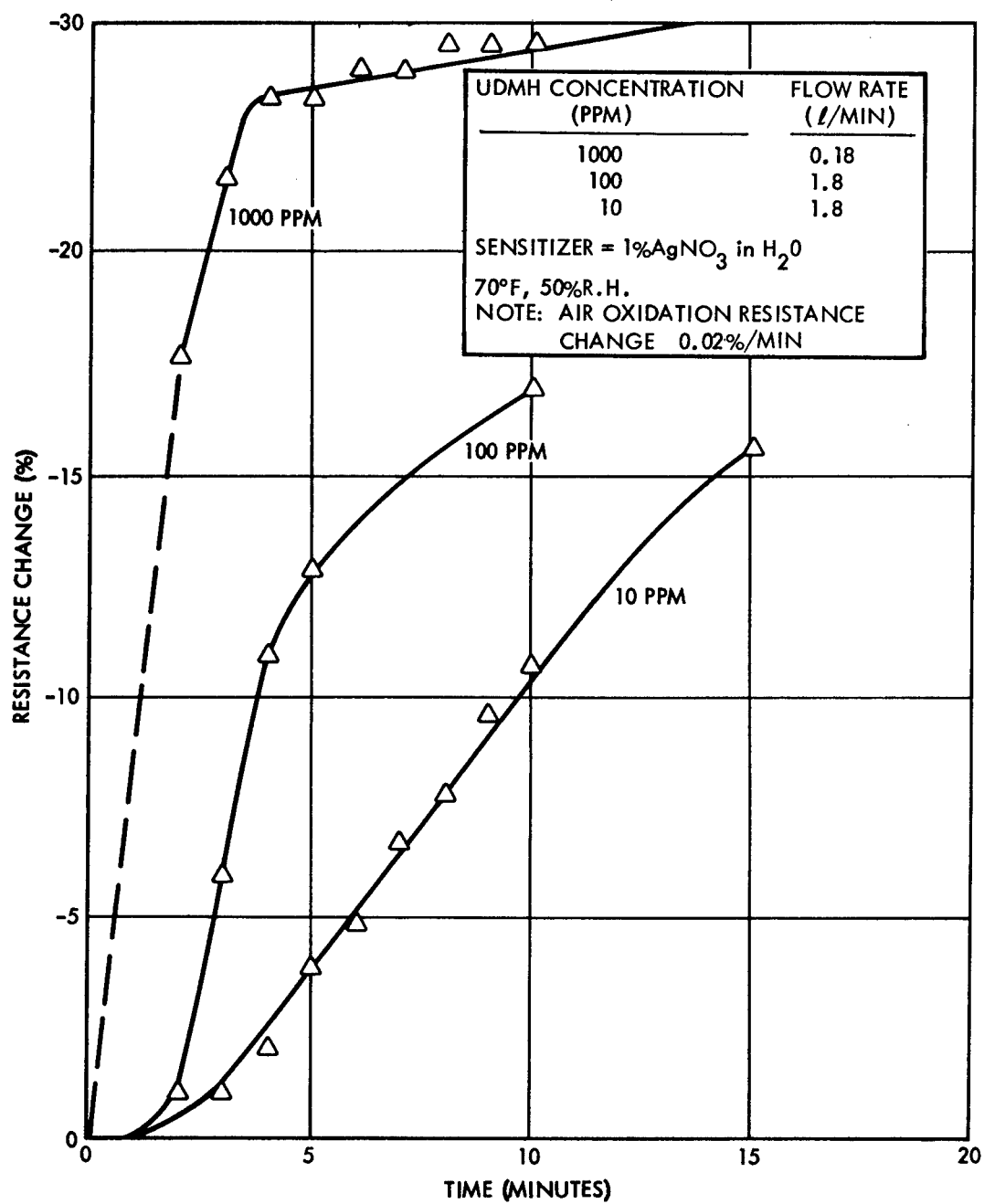


Figure 27. Percent Change of Resistance of Silver Films Exposed to UDMH—AgNO₃ Sensitizer

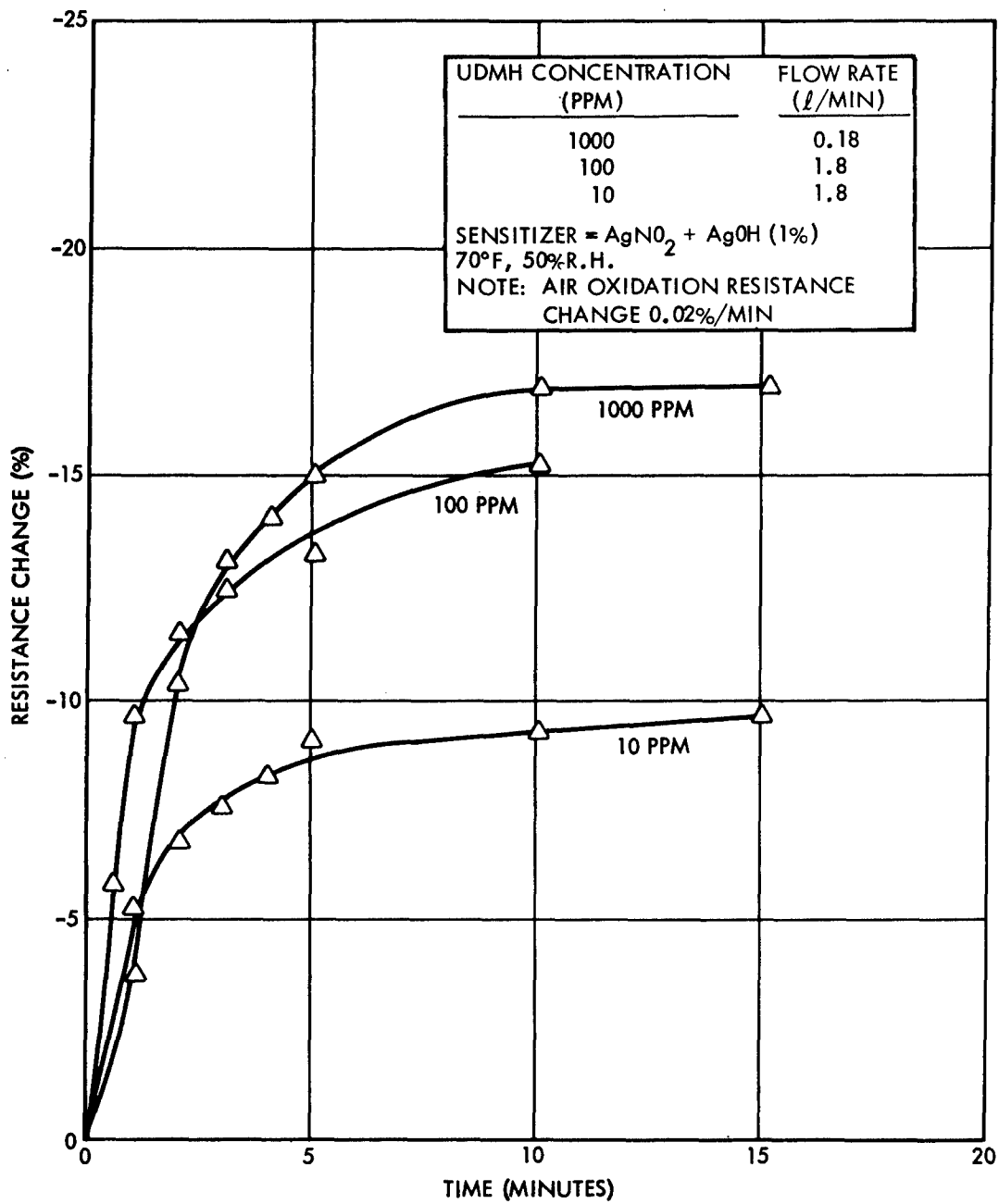


Figure 28. Percent Change of Resistance of Silver Films Exposed to UDMH— AgNO_2 - AgOH Sensitizer

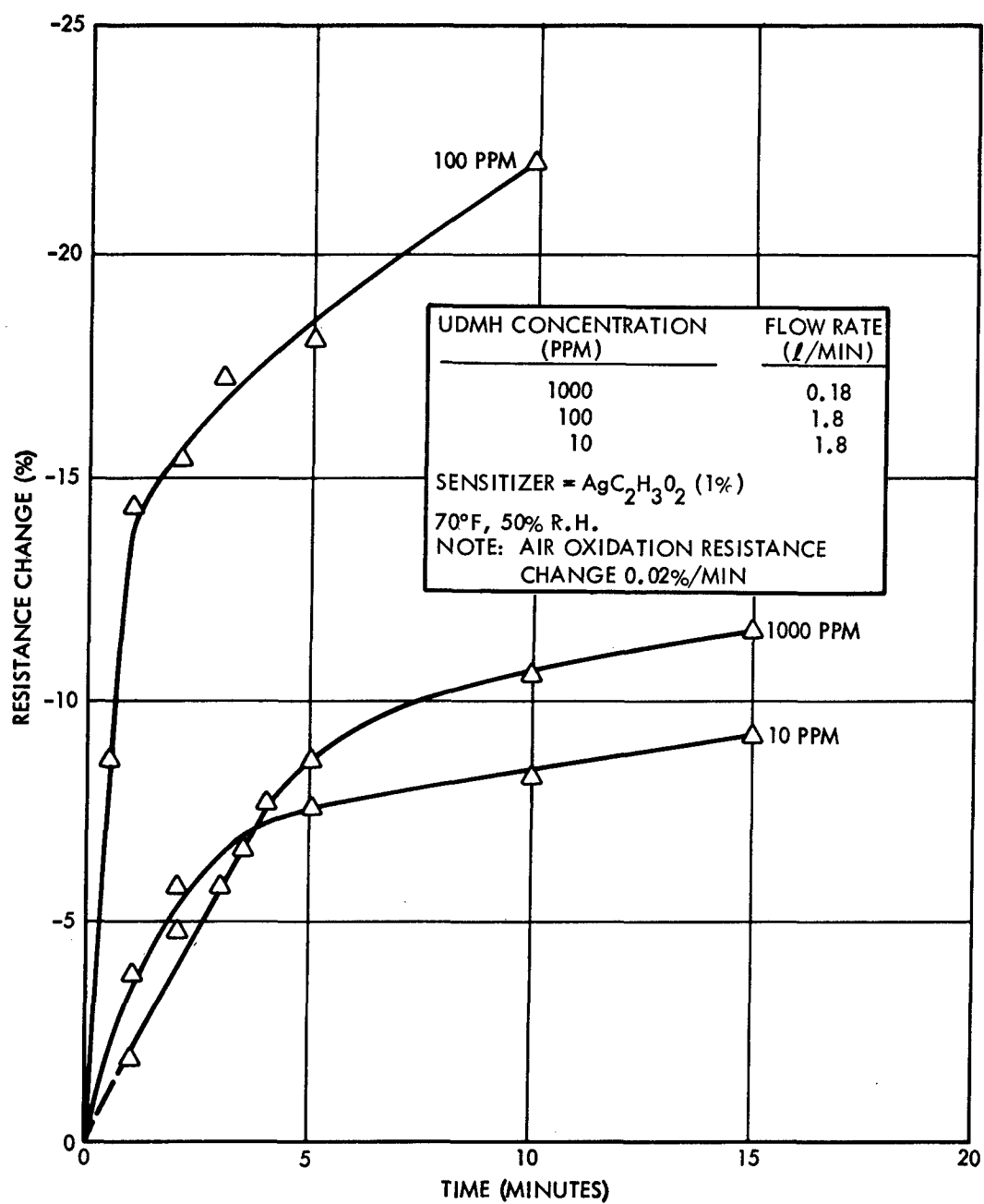


Figure 29. Percent Change of Resistance of Silver Films Exposed to UDMH— $\text{AgC}_2\text{H}_3\text{O}_2$ Sensitizer

Table XIV. Effect of Air Exposure on Sensitized Silver Films

Time of Exposure	Mean Response in Air (% change of resistance) When Sensitized by		
	1% AgNO ₃	1% AgAc	1% AgNO ₂ -AgOH
3 hours	0.7	6.2	5.9
24 hours	2.4	11.1	12.6

Table XV. Percent Change in Resistance of Films Exposed to UDMH after Aging 24 Hours in Air

Time of Exposure	Mean Response to 100 PPM UDMH (% change per minute) When Sensitized by			
	1% AgNO ₃	1% AgC ₃ H ₃ O ₂	1% AgNO ₂ -AgOH	No Sensitizer
5 minutes	0.6	0.0	0.1	0.0
10 minutes	0.9	0.0	0.2	0.0

Since many silver salts are photosensitive, we suspected that the aging effect may have been the result of a photoreaction. The effect of light on the initial resistance change in clean air was measured. Films were exposed to the humidified air in the dark and in ambient light and, as table XVI shows, lower rates of percent resistance change were observed for the films kept in the dark. The difference in rates attributable to the effects of light, however, was only a portion of the total change, and the observations cannot be explained wholly on the basis of photosensitivity of the film-sensitizer preparations.

Table XVI. Effect of Light on the Response of Sensitized Films in Air

Time of Exposure	Mean Response in Air (% change of resistance) When Sensitized by					
	1% AgNO ₃		1% AgC ₂ H ₃ O ₂		1% AgNO ₂ -AgOH	
	In Light	In Dark	In Light	In Dark	In Light	In Dark
3 hours	0.8	0.0	7.6	3.5	7.0	3.6
24 hours	2.7	0.9	14	5.2	15	8.9

Gold films were also investigated as conductive substrates for the UDMH sensor. As with the silver film, the gold films were coated with salts that theoretically would be readily reduced by UDMH. As shown in table XVII, good response was obtained with the salts AgNO₃ (12 percent change in resistance in 10 minutes), KAuCl₄ (11 percent change in 10 minutes), and AuI (6 percent change in 10 minutes). Although the gross changes observed with salts on gold films were not as great as those on silver films, the background rates for the gold films in clean air were significantly less than the background rates of silver films; e.g., gold films coated with KAuCl₄ (1 percent) salt when exposed to normal laboratory air had a resistance change of 2 to 3 percent per hour but showed an 11 percent change in resistance in 10 minutes when exposed to 100 ppm UDMH. In order to compare data for UDMH and other gases, the response data for gold films with KAuCl₄ sensitizer were calculated in terms of exposure factor and are presented in table XVIII. A 10-minute exposure to 100 ppm UDMH resulted in a 2.3 exposure factor. Figure 30 shows the mean response of these films in terms of exposure factor versus time.

Several materials were evaluated before a suitable coating for the reference side of the UDMH sensor was found. These included several types of tapes, lacquers, butyl and silicone rubber coatings, and various suspensions of inert chemicals, such as Teflon. The coatings were evaluated by first exposing sensors with a test coating on the reference

Table XVII. Response of Gold Films Treated with Various Sensitizers to 100 PPM UDMH

Sensitizer	Maximum Response Rate		Total Resistance Change			
	Time (min)	% Change per min	Time (min)	(%)	Time (min)	(%)
KAuCl ₄ , 1% aq.	7	0.3	5	0.6	10	1.2
	1	0.8	5	1.6	10	4.1
	5	1.4	5	5.0	10	11
TeCl ₄ , 1% aq.	3	0.2	5	0.2	10	0.2
AgNO ₃ , 1% aq.	14	0.6	5	1.2	10	2.4
	7	20.2	5	0.9	10	1.3
	1	0.9	5	4.4	10	5.3
AgNO ₃ , 5% aq.	1	2.0	5	6.9	10	12
	20	2.9			15	20
AgNO ₃ , 5% in MeOH	4	0.5	5	1.9	10	3.3
AgNO ₂ -NH ₃ , 1% aq.	5	0.5	5	0.7	10	1.6
	5	0.5	5	1.0	10	4.0
	4	0.5	5	1.9	10	2.8
AgNO ₂ -NH ₃ , 5% aq.	16	0.7	5	1.4	10	2.7
	4	0.3				
AuI, 1% in KI (aq.)	7	1.2	5	2.4	10	6.0
	4	0.5	5	1.8	10	3.7
AuI, 5% in KI (aq.)	4	0.5	5	1.8	10	4.0

Table XVIII. Response of Gold Films Sensitized with
1% AuCl_4 to 100 PPM UDMH

Average Maximum Response Rate		Total Resistance Change		
% Change/ Minute	Exposure Factor	Time (minutes)	% Change	Exposure Factor
0.8	0.08	5	2.6	0.38
		10	5.4	2.3

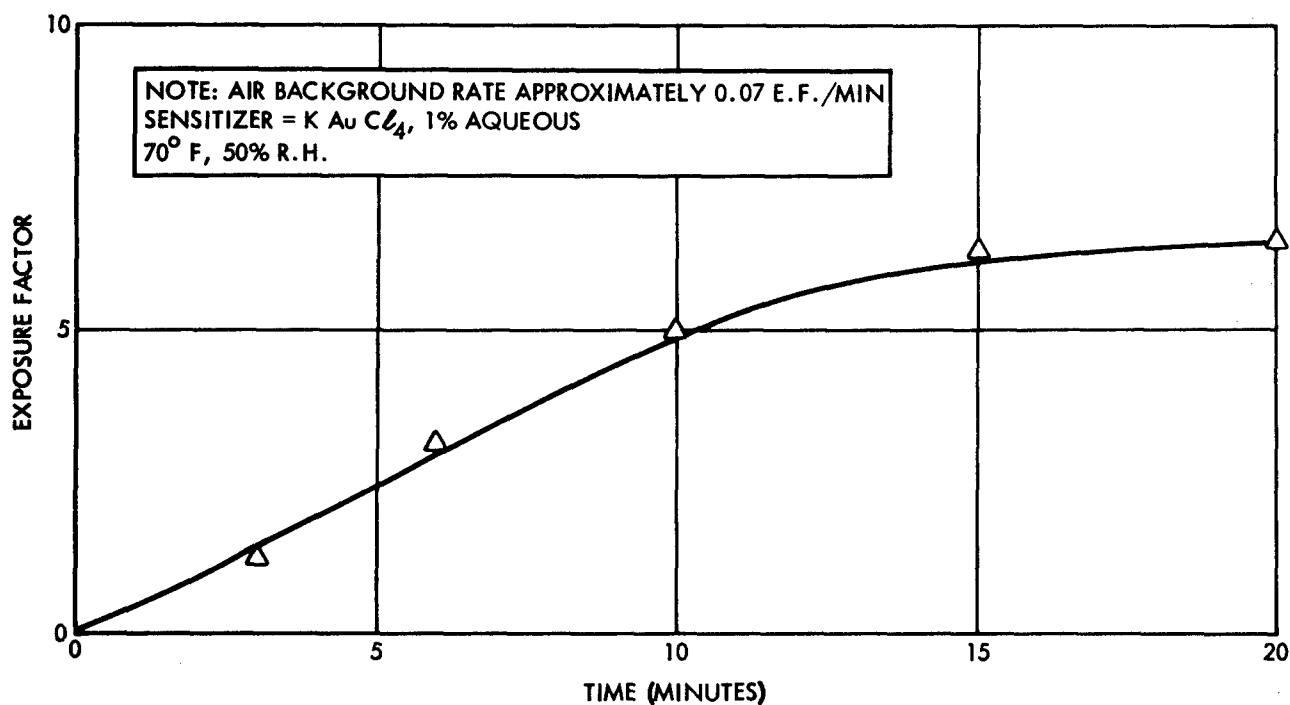


Figure 30. Exposure Factor of Gold Films Exposed to 100 PPM UDMH

half of the film to clean 50 percent R.H. air. The results are summarized in table XIX. Coatings which resulted in 0 or negative resistance changes were judged satisfactory, on the basis that since the resistance of the exposed side increases slowly because of corrosion in air, an apparent decrease in resistance of the coated side should be observed. As a result of the screening of materials, Scotch cellophane tape, vinyl tape, and Mystic tape were chosen for further studies to determine their permeability to UDMH. These coatings were compared by placing one type of coating on the reference side and one on the test side of the sensor and exposing the sensors to UDMH. The relative permeability of the coatings was evaluated by comparing the attack of one side relative to the other. The results, shown in table XX, indicate that Scotch clear cellophane tape is the least permeable to UDMH.

BREADBOARD INSTRUMENT

A breadboard readout instrument that can be handled easily by one person and that sounds an automatic alarm has been designed and fabricated for use with the thin film sensors. Schematic diagrams of the instrument and alarm circuits are shown in figures 31 and 32. A picture of the instrument with a sensor located in a remote holder is shown in figure 33. The instrument uses a bridge type of circuit, with the sensor forming two legs of the bridge. When the sensor resistance changes, the bridge becomes unbalanced. This unbalance is amplified by a miniature solid state operational amplifier, which drives a meter relay. At a preset exposure level the meter relay operates an audible alarm to give a warning of exposure.

This instrument has an internal check circuit which switches in a dummy sensor with a preset unbalance of one exposure factor to determine if the instrument is functioning properly. With the input switched to the dummy sensor, the bridge current is adjusted by means of the three-turn potentiometer to give a reading of one exposure factor on the meter. After this adjustment is made the input is switched to the measuring sensor, and the bridge is balanced by means of the zero-adjust dial to give a zero reading on the meter. When the sensor is exposed, the meter reads the total exposure in units of exposure factor as defined previously.

Table XIX. Protective Characteristics of Various Coatings for Use on Films^(a)

Sample No.	Coating	Total % Change of Initial Resistance in Air ^(b)		
		Initial Change	3 Hours	24 Hours
13	Vinyl tape (coated prior to test)	--	0.0	nil
14	Vinyl tape (coated prior to test)	--	0.0	-0.9
	Vinyl tape (coated prior to test)	--	--	--
15	Vinyl tape (applied fresh)	0.0	nil	1.4
16	Vinyl tape (applied fresh)	-1.6	0.8	0.0
17	Scotch tape (clear)	-2.5	-2.4	-4.0
8	Scotch tape (clear)	-2.0	-5.0	-3.0
9	Krylon clear acrylic	0.0	nil	nil
10	Teflon (fluoroglide spray)	-18	0.9	9.3
7	Na ₂ SiO ₃ , 10 percent	-10	2.3	3.7
8	Na ₂ SiO ₃ , 50 percent	-5.9	0.9	1.4
11	Collodion (EtO-MeOH solution)	37	0.0	1.3
1	Pro-Seal butyl rubber (applied prior to test)	--	1.8	6.2
20	Pro-Seal butyl rubber (applied prior to test)	--	2.4	7.8
2	Pro-Seal butyl rubber (applied fresh)	6.6	2.5	6.2
4	Paraffin	0.9	2.2	8.7
29	Silastic silicone rubber	2.6	0.0	0.0

(a) Substrate, Ag film; conditions, room temperature and 50 percent R. H.

(b) Positive change indicates increase in resistance of coated (reference) side of film. Three-hour and 24-hour figures were corrected for initial change.

Table XX. Permeability of Coatings to UDMH^(a)

Reference Side Coating	Test Side Coating	Time (hours)	Percent Change of Resistance ^(b)
Vinyl tape	Scotch tape	18	5.1
		18	3.5
		2	0.0
		2	nil
Vinyl tape	Mystic tape	2-1/2	2.3
		2-1/2	2.4
Mystic tape	Scotch tape	2-1/2	0.8
		2-1/2	1.1

(a) Concentration of UDMH = 100 ppm.

(b) Positive change indicates greater permeability of reference side over test side.

When a full scale reading of 1, 5, or 10 exposure factors is reached an audible alarm sounds. At any time during a measurement the instrument can be switched to the calibrate position to check the operation without disturbing the measurement. After slight exposures to low concentrations of the gases being detected, the meter may be re-zeroed and new measurements can be made. When the instrument can no longer be zeroed, the sensor should be replaced. If the sensor is removed while the instrument is in operation, or for some other reason is damaged, a full-scale deflection of the meter occurs immediately, with the resultant sounding of the alarm. Replacing the sensor will make the instrument operational again. The system is therefore a fail-safe device.

Two calibrate and two operate positions are provided on the instrument, one labeled NO₂ and one labeled F₂. The instrument must be calibrated separately for these sensors due to differences in the initial film resistance. The F₂ position is also used for UDMH sensors. The operation of the two calibration adjustments is completely independent; therefore the F₂ calibration need not be in adjustment to use an N₂O₄ sensor. Further details are provided in the operating instructions for the instrument published separately from this report.

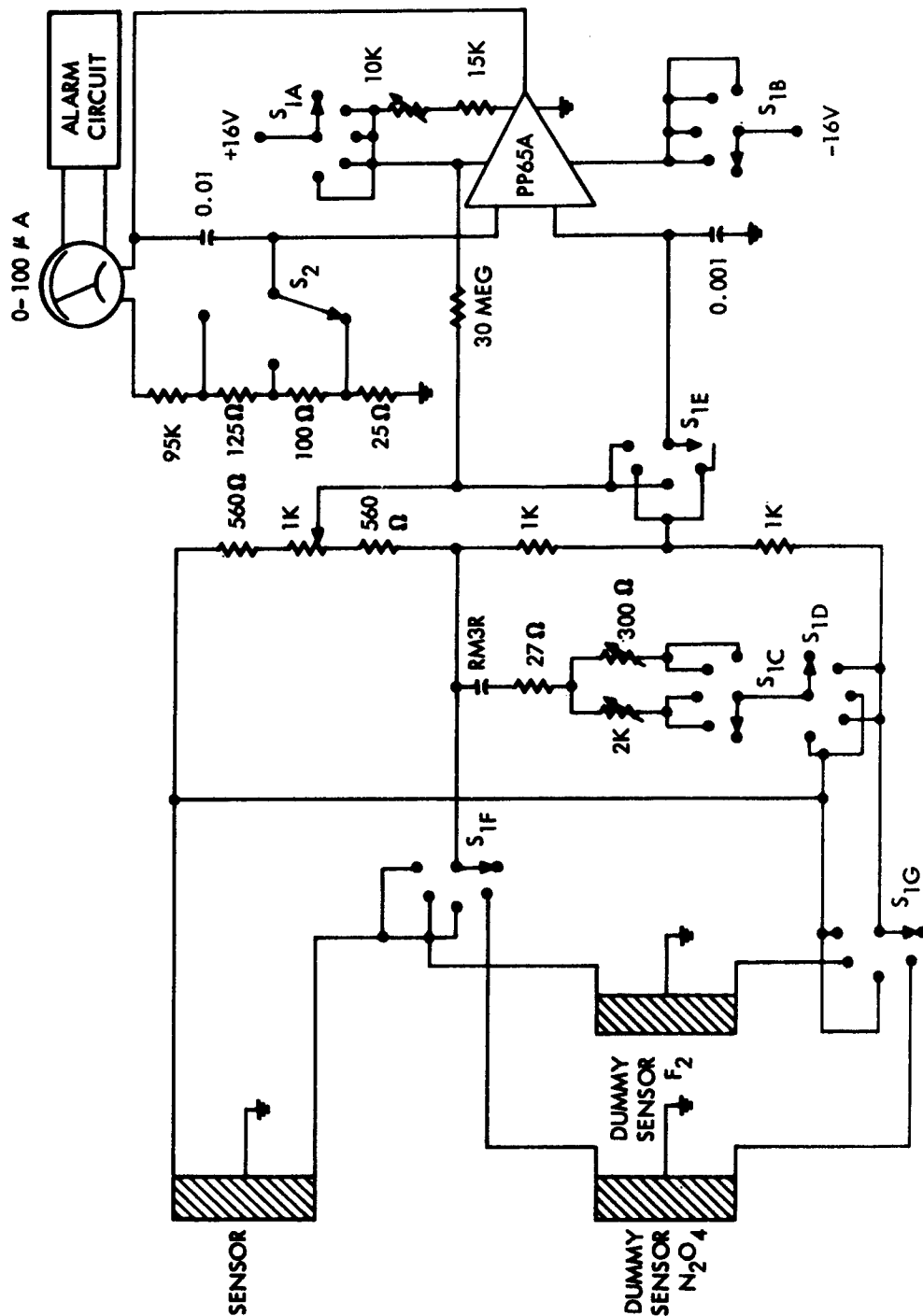


Figure 31. Breadboard Instrument Circuit

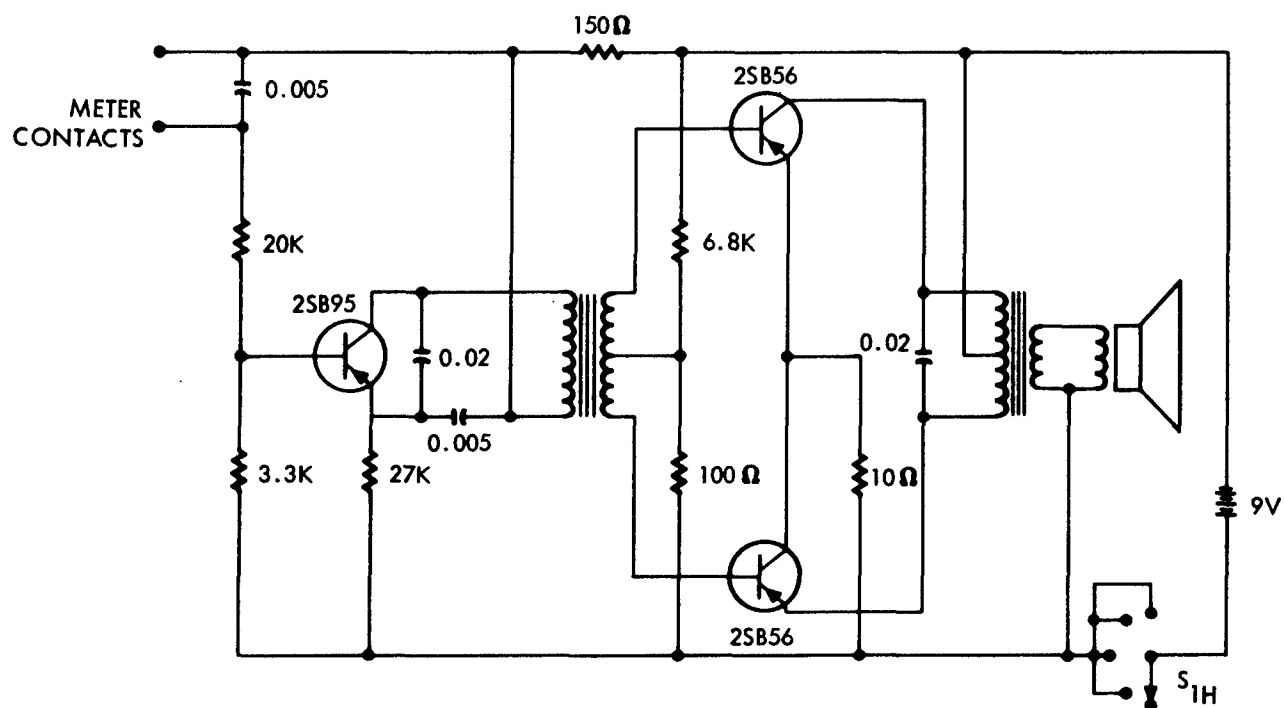


Figure 32. Alarm Circuit



Figure 33. Breadboard Instrument

SECTION IV

CONCLUSIONS

From the results presented in this report, it can be concluded that, by means of strict control of the production and sensitization techniques, the response of the sensors can be controlled to ± 20 percent. It can also be concluded that the effect of temperature on the response is less than 20 percent in most cases and can be compensated under conditions where it is large enough to be a problem. Table XXI summarizes the present performance characteristics of the sensors. The sensor materials selected for the three vapors are KCl on silver films for N_2O_4 detection, KBr on copper films for fluorine, and $KAuCl_4$ on gold films for UDMH detection.

Table XXI. Performance Characteristics of Sensors

Toxic Vapor	Sensor Composition	Concentration Range (ppm)	Reproducibility
N_2O_4	0.1% KCl on Ag Film resistance 70 ohms	0.1 to 50	<20%
Fluorine	2% KBr on Cu Film resistance 30 ohms	1.0 to 100	25%
UDMH	1% $KAuCl_4$ on Au Film resistance 10 ohms	10.0 to 1000	Undetermined

SECTION V

RECOMMENDATIONS

While much progress has been made in improving the performance of the sensors, our results suggest that large improvements can still be achieved in the sensitivity and reproducibility, storage life, and stability to humidity and temperature of the sensors. These improvements do not require any fundamental changes in concept but rather improvements in the art of preparing the sensors. Methods of improving the performance of the sensors to the point where both oxidants and fuels could be detected at concentrations of 0.1 ppm within 5 minutes after exposure of the sensor to the environment are suggested below. Furthermore, sensors could be so constructed that humidity variations over the range 20 to 90 percent R.H., temperature variations from -10° to $+50^{\circ}\text{C}$ (0° to 120°F) and light exposure from direct sunlight to normal room lighting would not cause significant errors.

The recommended program includes a study of improved methods for preparing the films, possible development of sensors for NF_3 and OF_3 in addition to F_2 , N_2O_4 , and UDMH, methods of improving sensitivity and stability, and methods of providing humidity and temperature compensation.

We believe that the feasibility and convenience of these sensors has been amply demonstrated and that we are now at a point where special techniques must be developed for constructing sensors with the characteristics which our investigations to date have shown to be necessary. This effort will result in a small, portable detection system, which will be useful for early-stage warnings and inexpensive enough that each individual in critical areas can have his own personal detector.

On the basis of the results reported, we recommend that follow-on studies be carried on in four separate areas:

Area I Development of manufacturing procedures to produce films that provide suitable response by use of latest state-of-the-art improvements in film-deposition methods and sensitizer development.

- Area II Continuation of the basic development studies in order to expand the usefulness of the system by developing sensors for other vapors and by improving the existing sensors.
- Area III Development of detection systems that are unaffected by variations in atmospheric conditions.
- Area IV Design and construction of a breadboard instrument representing the latest state-of-the-art in electronic circuitry.

Area I

Procedures for the production of films by vacuum deposition and also by alternative methods, such as the silk screening of metal particles, should be developed. The optimum evaporation temperature, pressure, and time for vacuum-deposition of uniform reactive films of the sensor materials should be determined. Vacuum-deposition facilities available at TRW allow much greater control of these variables than has been possible under the previous contracts.

Alternative methods of thin-film production, such as silk screening and electrodeposition, should be evaluated to determine if they would increase sensitivity, response to vapors, stability, and reproducibility. Since our facilities are in the immediate vicinity of the TRW semiconductor manufacturer facility, the very precise silk-screening techniques it has developed could be used for the alternative technique.

Production methods of applying sensitizer materials to the surface of thin films so that optimum performance is obtained should also be tested. A new technique to be tested is the vacuum-deposition of the salt layer where such a procedure is practical. Refinements in the dipping process and prepackaged film-activator should also be tested.

Area II

The purpose of Area II would be to develop sensors for other vapors and to expand the usefulness of the present sensors by increasing sensitivity and operating ranges.

Basic reaction mechanisms should be studied, with the aid of analytical tools such as X-ray diffraction. Information gained from these basic studies could be used to predict response to other vapors and to provide insight into possible methods of improving the performance of

both previously developed and new sensors. Parameters to be considered in improving performance include the effects of atmospheric variables, including sunlight on background, and response rates.

The reactivity of NF_3 , OF_2 , and other gases with various metals and salts should be determined, and promising sensor materials will be screened for response to these vapors. The effects of temperature, humidity, and sunlight on response should be determined and means of compensating for these environmental effects studied.

Area III

Methods of improving sensor sensitivity and shelf-life to provide a stable sensor of the desired sensitivity should be evaluated. Methods to accomplish this should be selected from among those outlined in this report and those arising from studies in Area I. Design information for the production of large quantities of films with the desired response characteristics should be developed.

Methods of achieving the necessary temperature and humidity compensation in the final design of the sensor systems and/or protecting the sensors from the effects of sunlight should be considered. The use of artificial environments and electronic means of compensation should also be investigated. Breadboard circuits for electronic compensation will be assembled and evaluated.

Any of the previously mentioned developments that prove worthy should be incorporated to a prototype system incorporating the latest developments in sensor technology including temperature, humidity, and light control, as well as electronic compensation for the effects of these variables. Close liaison should be maintained with the contracting engineer to ensure that the detector system is designed to fulfill the primary requirements for field use. Miniature personnel systems, portable area monitors, and leak detection systems should be considered. Final selection of the type of system will depend on the progress made in the development of new technology, as well as upon the requirements of the contracting agency.

Area IV

Area IV will be the fabrication and delivery of a complete prototype monitoring system that utilizes the latest state-of-the-art developments in sensors for the vapors being investigated and the latest developments in readout instrument design.

GLOSSARY

Resistance. The electrical resistance of a metal film as measured with a standard ohmmeter. Initial resistance is the electrical resistance of a metal film before it is subjected to any chemical treatment or exposure to any reactive vapor.

Resistance Change. A change in electrical resistance of a metal film due to a change in the chemical or physical structure of part of that film. Resistance change is expressed as a percent of the initial resistance.

Exposure Factor. A numerical value, derived from the resistance change and the initial resistance, which approximates the amount of metal that has undergone a chemical change.

Exposure. Contact of a metal film with air containing a known quantity of a reactive vapor of interest for a known length of time.

Response. A change in a metal film caused by contact with a reactive vapor. The response may be expressed as resistance change or as exposure factor.

Response Rate. A time rate of change of a metal film caused by contact with a reactive vapor. The response rate may be expressed as percent resistance change per minute or as exposure factor per minute.

Background. A change in chemical or physical structure of a metal film when in contact with clean air containing no reactive vapor. Background may be expressed as resistance change or as exposure factor.

Background Rate. A time rate of change of a metal film that occurs during contact with clean air containing no reactive vapor. The background rate may be expressed as percent resistance change per minute or as exposure factor per minute.

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13. ABSTRACT The subject of this report is the development of a portable system for the detection of low concentrations of nitrogen tetroxide (N ₂ O ₄), fluorine (F ₂), and unsymmetrical dimethylhydrazine (UDMH) in air. The detection system is based upon the change of electrical resistivity of thin metal films when exposed to these gases. Silver metal films coated with appropriate salts proved to be applicable to the detection of all three gases; however, the following sensitized metal films were found to be optimum: for N ₂ O ₄ , silver; for F ₂ , copper; and for UDMH, gold. Using the best film and salt combinations found to date, N ₂ O ₄ could be monitored over the range of 0.1 to 50 ppm, F ₂ over the range 1.0 to 50 ppm, and UDMH over the range 10 to 100 ppm, with a standard deviation of about 20 percent. The effects of temperature over the range 50° to 90°C and of humidity from 10 to 90 percent on the response characteristics of the thin film sensors were found to be significant but within the tolerance limits. Means for reducing these effects were suggested which, if successful, would, in effect, make this detection system practically independent of changes in the environment. A portable breadboard readout instrument was designed and fabricated for use with the sensors to form an integrated detection system for personal protection.			

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Detectors Toxic Vapor Detection Personnel Protection Dosimeters						

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